

THERMODYNAMIC MODELING OF PH IN CITRUS SIMULATION SYSTEMS
UNDER HIGH PRESSURE CARBON DIOXIDE

By

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To my wife, parents and brother

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KEY TO SYMBOLS

SYMBOL	DEFINITION	UNITS
μ	Chemical potential	J/mole
A	Helmholtz free energy	J
n	Moles	moles
T	Temperature	°C
V	Molar volume	cm ³ /mole
V°	Standard molar volume	cm ³ /mole
P	Process pressure	MPa
P°	Standard pressure	MPa
ΔV	Change of molar volume	cm ³ /mole
ΔV _R	Change of reaction volume	cm ³
κ^0	Standard isothermal compressibility coefficient	cm ³ /mole.KPa
v	Stoichiometric coefficient	(dimensionless)
K	Equilibrium constant	moles/cm ³
a	Activity	moles/cm ³
γ	Activity coefficient	(dimensionless)
γ ^c	Combinatorial activity coefficient	(dimensionless)
γ ^R	Residual activity coefficient	(dimensionless)

X	Molar concentration	moles/cm ³
R	Ideal gas constant	J/g.mole.K
a _r	Ionic radius	Angstroms
μ_1	Ionic strength	moles/cm ₃
Z	Ionic charge	(dimensionless)
x	Mole fraction	(dimensionless)
v _k	Group numbers	(dimensionless)
R _k	van der Waals volume parameter	(dimensionless)
Q _k	van der Waals surface parameter	(dimensionless)
θ_m	Group surface area fraction	(dimensionless)
X _m	Group fraction	(dimensionless)
a _{nm}	Group interaction parameter	J
Ψ_{nm}	Exponential of group interaction parameter over temperature	exp(J/K)
S	Solubility	moles/cm ₃
x _{iu}	Coded design variable	(dimensionless)
X _{iu}	Design variable	---
X _{i,m}	Mean of design variables	---
S _i	Scale factor	---
t	Test statistic	---
H ₀	Null hypothesis	---
H _a	Alternative hypothesis	---
d _{avg}	Average difference between treatment means	---

μ_d	Difference between treatment means	---
S_d	Standard deviation of paired differences	---
r	Coefficient of correlation	(dimensionless)

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Thermodynamic models were developed to predict the pH of liquid citrus simulation systems as functions of high pressure carbon dioxide process conditions. Such processing holds promise as an alternative to heat pasteurization for inactivating pectic enzymes through temporarily lowering pH instead of using heat. Predicted pH values were compared with those measured experimentally at different process conditions with the aid of a pH probe especially designed to withstand high process pressures. The four simulation systems included pure water-carbon dioxide, ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide and ascorbic acid-citric acid-water-carbon dioxide. Gage process pressures ranged from 0 to 34.50 MPa at temperatures of 32, 37 and 42°C. Acid concentrations ranged from 0 to 1.107×10^{-3} M and 0 to 6.080×10^{-4} M for ascorbic and citric

acids, respectively. For all the simulation systems the predicted pH values closely followed the measured pH values. In the pure water-carbon dioxide system, the pH was a strong function of process pressure but a weak function of process temperature. In the ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide and ascorbic acid-citric acid-water-carbon dioxide systems, however, the pH was relatively insensitive to pressure while remaining a strong function of acid concentrations.

The pH in the ternary and quaternary simulation systems showed a very small variation over the experimental pressure range, indicating that low pH alone can not totally account for pectinesterase inactivation in citrus juice treated with supercritical carbon dioxide. Since the pH variation was greater in the water-carbon dioxide system than the other three systems, more carbon dioxide was dissolved in the binary system resulting in the generation of greater quantities of carbonic acid in the solution. The reduction in the solubility of carbon dioxide in the solution was believed to be caused by the presence of other ions that formed as a result of dissociation of ascorbic and citric acids in the ternary and quaternary systems.

CHAPTER 1 INTRODUCTION

The cloud in citrus juice is responsible for most of the characteristic color and appearance that is widely recognized and appreciated by consumers. The retention of this cloud in most citrus juices, concentrates and beverages is of prime importance to the citrus-processing industry for consumer acceptance. Most of the published work relating to the cloud loss in citrus juice products attributes the loss mainly to the activity of the pectic enzymes, particularly pectinesterase naturally present in the juice (Baker, 1977). Part of the methylester linkages of the soluble pectin is split by pectinesterase, resulting in the formation of low-methoxy pectin which, in the presence of calcium and magnesium cations, precipitates and results in the cloud loss. Divalent cations must be present in solution for the pectin molecules to agglomerate and subsequently settle out (Rouse and Atkins, 1952).

Most procedures for prevention of cloud loss are based on heat inactivation of pectinesterase by pasteurization (Rouse and Atkins, 1952; Rouse and Atkins, 1953; Mizrahi and Berk, 1970; Versteeg et al., 1980; Wicker and Temelli, 1988). However, pasteurization temperatures can result in

flavor and aroma changes, as well as color changes due to nonenzymatic browning.

Owusu-Yaw et al. (1988) have shown that pectinesterase can also be inactivated by lowering the pH of the juice using either a cation exchange resin or by direct addition of hydrochloric acid to the orange juice. Treatment with supercritical carbon dioxide has been recently proposed as a promising alternative process for inactivating pectinesterase and improving cloud stability (Arreola, 1990). Cloud stability in this process is based on the hypothesis that under pressure carbon dioxide dissolves in the solution producing carbonic acid, thereby temporarily lowering the pH and inactivating pectinesterase. Arreola (1990) showed that pectinesterase was inactivated in the supercritical process with various combinations of pressure, temperature and process time.

Studying the variation of pH during the supercritical process provides the means of better understanding how pectinesterase is inactivated in this process. Also, for carbonated beverages it is important to know what the pH variation is during the carbonation process as well as when it is packed under pressure (Moore and Buchanan, 1930).

Citrus juices and beverages, with their complex composition, can be viewed as electrolyte solutions of multiple ions. During the supercritical process, the pH varies with the process pressure, temperature and solution

composition. From the chemical process design point of view, the studies of food electrolyte solutions and applications of the supercritical carbon dioxide process to these systems have rarely been done in the past (Maurer, 1983). In the supercritical carbon dioxide process, through the use of reaction equilibria, the pH of the solution may actually be calculated at specific process conditions. This involves finding a mathematical expression (model) for the pH as a function of the process conditions using thermodynamic relations and available data.

The objectives of this study were to

- (1) Develop thermodynamic models to predict the pH of four citrus simulation systems of (a) pure water-carbon dioxide , (b) ascorbic acid-water-carbon dioxide, (c) citric acid-water-carbon dioxide and (d) ascorbic acid-citric acid-water-carbon dioxide.
- (2) Test the models by comparing the predicted pH with the actual measured pH values for each system at different process conditions.

- (3) Determine significance of pH lowering in pectinesterase inactivation and subsequent citrus cloud stability by studying variations in pH over the experimental pressure range at different temperatures and system compositions.

CHAPTER 2 REVIEW OF LITERATURE

2.1 Supercritical CO₂

2.1.1 Properties and Applications

Supercritical carbon dioxide processing is a unique unit operation that utilizes the special properties of the solvent carbon dioxide above its critical temperature and pressure. The development of the supercritical process technology has largely been based on practical experience and engineering intuition. The process can perform different operations, depending on the nature of the starting material, the operating conditions, and the supercritical solvent (Rizvi et al., 1986a). Each of these factors must be carefully considered before proceeding with the development of a successful supercritical process.

Carbon dioxide has a critical temperature of 31.1°C and a critical pressure of 7.38 MPa (McHugh and Krukonis, 1986). Within the supercritical region carbon dioxide exhibits its special properties such as low viscosity, low surface tension, and high diffusivity (de Fillippi, 1982). In this region, carbon dioxide exhibits physicochemical properties intermediate between those of liquids and gases, which enhances its role as a solvent. Its relatively high density results in its good solvent power, while its relatively low

viscosity and diffusivity provide appreciable penetrating power into the solute matrix. Chrastil (1982) experimentally observed that the concentration of a solute dissolved in a supercritical fluid is related to the density of the fluid, raised to some positive power. This observation, coupled with the pressure-density-temperature behavior indicates that the greatest solubility-pressure and solubility-temperature variations occur in the region near the critical point of the solvent. As the temperature increases within this region, the density of the solvent decreases rapidly, and the solubility of a solute would be expected to decline despite its increased vapor pressure. At very high pressures, however, the vapor pressure of the solute varies more strongly with temperature than the density of the solvent. Thus, the solubility of a solute increases with increasing temperature at high pressure. Similarly, a decrease in the solvent power of a compressed gas can be expected when pressure is reduced. These rough qualitative conclusions from the density-pressure behavior of a solvent were discussed by Kurnick et al. (1980; 1981) working on the solubility of benzoic acid in carbon dioxide.

The chemical complexity of most food ingredients and their vulnerability to react and degrade at elevated temperatures emphasize the considerations that must be taken into account in supercritical solvent selection. Because of its unique properties, carbon dioxide has a wide range of

food processing applications. It is an inert, nonflammable, nontoxic and nonexplosive substance with a moderate critical pressure which minimizes compression costs. Among the many applications of supercritical carbon dioxide, extraction and fractionation cover a good percentage. They include decaffeination of coffee, recovery of hop extracts and oil and fat removal applications (Bott, 1982; Vollbrecht, 1982; Calame and Steiner, 1982; Gardner, 1982).

Beyond extraction and fractionation, carbon dioxide has considerable antimicrobial activity. The degree of inhibition, as reported by Clark and Takacs (1980), depends on the type of microorganism. *Pseudomonas* appear to be very sensitive while other types of organisms such as *lactobacilli*, yeasts, and *clostridia* are less sensitive (Jones and Greenfield, 1982; Molin, 1983). Carbon dioxide also acts synergistically with certain antimicrobial agents such as sorbate (Haas and Herman, 1977a) and propylene glycol (Haas and Herman, 1977b).

The inhibitory effect of carbon dioxide has also been reported to increase when it is applied under pressure (Kauffman et al., 1969; Enfors and Molin, 1978, 1980; Blickstad et al., 1981; Doyle, 1983; Kamihira et al., 1987). Haas et al. (1989) determined that the moisture content (or water activity, a_w) of the product was very important to the antimicrobial action of CO_2 in wheat flour, while the temperature of exposure was not. There was slightly less

effect at -22°C than at 23°C and 50°C . Haas et al. (1989) also performed experiments with freshly squeezed orange juice (pineapple variety) and reported that the microflora consisting of gluconobacter, yeast, mold, and lactic acid bacteria were completely eliminated at a pressure of 5.516 KPa. Although not much data are available on the inactivation of pectinases by carbon dioxide, Haas et al. (1989) reported a 24-48 hour delay in flocculation of orange juice cloud. They speculated that either pectinases may be inactivated at a pressure of 5.516 KPa or it could be that some of the CO_2 remains bound to the cloud affecting its specific gravity.

2.1.2 Thermodynamic Models of Phase Equilibria

Mixtures of materials at supercritical conditions exhibit highly nonideal behavior and do not lend themselves easily to quantitative data correlation and phase equilibrium predictions. This is particularly true for materials of biological origin, because their physical property data are usually extremely scarce-- if available at all (Rizvi et al., 1986b).

Models of equilibrium between supercritical and condensed phases can be separated into two general classes: those describing supercritical fluid-liquid equilibria and those describing supercritical fluid-solid equilibria. As with all other equilibria, the condition for equilibrium is

that the chemical potential (μ_i) of each component i in one phase be equal to the chemical potential of that component in all other phases, that is,

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\omega \quad (2-1)$$

where $i=1,2,\dots,N$ for an N -component system in phases $\alpha, \beta, \omega, \dots$

The main differences between models of supercritical fluid-liquid and supercritical fluid-solid mixtures are that the solid phase is assumed to dissolve no solvent (Prausnitz, 1969; Gitterman and Procaccia, 1983; Procaccia and Gitterman, 1983), and in multicomponent systems, no solid solutions are assumed to form (Kurnick and Reid, 1982). These two assumptions simplify the analysis by eliminating the composition dependence of the chemical potential of the solid phase. In case of equilibrium between liquids and supercritical fluids, however, multicomponent solutions are common and considerable amounts of supercritical solvent can dissolve into the liquid phase (Brunner and Peter, 1982) leading to the composition dependence of the chemical potential.

2.1.3 Equations of State

Phase equilibrium calculations require a method for computing the chemical potential from available data. The chemical potential of any component i in a supercritical fluid or liquid phase α may be computed from the molar Helmholtz free energy A by means of the Dieters and Schneider (1976) relation:

$$\mu_i^\alpha = \left[\frac{(\partial A^\alpha)}{(\partial n_i^\alpha)} \right]_{T, V, n_{j \neq i}} \quad (2-2)$$

where the Helmholtz free energy is a function only of the pressure, volume, temperature and composition. Knowing the Helmholtz free energy at the reference state of a pure component and the chemical potential (calculated by an equation of state), the Helmholtz energy can then be predicted at the equilibrium state. Numerous process-oriented equations of state which describe high density fluids have been proposed. These equations vary in accuracy, number of parameters, and amount and type of data required to fix their parameters. Vidal (1983) and Gubbins (1983) offer good reviews of equations of state and mixing rules for their parameters. Pure-component equation of state parameters for materials for which pressure-volume-

temperature are unavailable may be back-calculated from phase equilibrium data. Mixture parameters are always back-calculated from binary or multicomponent phase equilibria data using nonlinear reduction techniques (Anderson et al., 1978, and Skjold-Jorgensen, 1983). Some of the commonly used equations of state include van der Waals, Redlich-Kwong (1948), Peng-Robinson (1976), and Teja-Patel equations (Rizvi et al., 1986b).

2.1.4 Liquid-Supercritical Phase Equilibrium Models

Models of liquid-supercritical phase equilibria can be classified into two types: those which treat the liquid phase as a dense gas, and those which treat the system as a classical liquid-vapor equilibrium. The first approach has been shown to be useful by van Krevelen (1968), who proved that the van der Waals equation of state could predict five out of the six known classes of fluid phase diagrams and predicted phase behavior that had not yet been experimentally observed. In this approach, an equation of state is used to describe both the liquid and supercritical phases, by computing the chemical potential from an equation of state for each component in the system. To apply these equations to biomaterials for which equations of state are unknown and critical data are not available, binary solubility data are used to obtain estimates of the equation of state parameters for the nonvolatile solute. Solute-

solvent interaction parameter(s) are estimated from solubility data, even if the equation of state parameters are unknown for the solute. To extend the calculation to ternary systems, the parameters obtained in the way just described, from binary data, may be used in conjunction with some ternary data to estimate the interaction parameters (Rizvi et al., 1986b).

This model has been shown to adequately represent vapor-liquid equilibria for numerous systems of hydrocarbons and low molecular weight molecules over a wide range in polarity and sometimes even close to critical points (Gray et al., 1970; Soave, 1972; Patel and Teja, 1982; Mollerup and Fredenslund, 1979). King et al. (1983) have used a modified Soave-Redlich-Kwong equation of state for applying the model to various binary systems involving triglycerides mixtures and fatty acids. Their results indicate generally good correlation between predicted and experimental phase equilibrium data, although precise experimental data is difficult to obtain in the supercritical region.

Correlations based on vapor pressure data (Joffe et al., 1970) and liquid molar volume (Brunner and Hederer, 1979) have been developed. These correlations permit relatively precise estimation of Redlich-Kwong pure-component equation of state parameters for heavy

biomaterials, such as long-chain fatty acids and triglycerides.

In the classical vapor-liquid equilibrium model, activity coefficients are used to correlate experimental data. Since activity coefficients are not required to have any compositional functionality, the method has the advantage that data which may not be used with an equation of state can be used with equations such as Henry's law equation to predict the behavior of the components (Prausnitz, 1969; Reid et al., 1977). From this point of view, if enough physical property data as well as activity coefficient data could be obtained from literature, this technique would provide a powerful and fundamentally valid way to correlate data, especially if the data cannot be adequately correlated by equations of state.

2.2 Pectinase Action and Citrus Juice Cloud

2.2.1 Pectic Substances and Pectic Enzymes

The pectic substances in the plant tissues and the enzymes which degrade them are of major importance to the food industry because of their effect on texture of food and in the preparation of wines and fruit juices. The application of enzymes in the production of fruit juices, extracts and concentrates, was first introduced by Kertesz (1930,1931), Willaman (1933) and Willaman and Kertesz (1931) in the United States. Although many articles have been

published in this area, the mechanism of action of pectinases is not fully understood. Kertesz (1930) reported that the cloudiness of fruit juices was partly due to their pectin content where the colloidally suspended pectin would hold other substances in suspension. Pectic enzymes (pectinases) have been designated by Kertesz as that group of enzymes which hydrolyze pectic substances into reducing sugars. Pectic (Greek=congealing) substances are a group of complex colloidal plant carbohydrates made up primarily of Alpha-(1-4)-D-polygalacturonic acid located mostly in the middle lamella between cells in higher plant tissues. Polygalacturonic acid exists in varying states of methoxylation and neutralization. Pectin is composed of polygalacturonic acid with about 75% of the carboxyl groups being esterified with methanol. Pectic acid is an almost pure, colloidal, polygalacturonic acid free from methoxyl groups. Normal or acid salts of pectic acid are called pectates (Willaman, 1933).

2.2.2 Classification of Pectic Enzymes

Pectinases can be divided into two categories: Depolymerizing enzymes and saponifying enzymes (or pectinesterases, P.E.). The depolymerizing enzymes are further classified according to: hydrolytic or transeliminative cleavage of glycosidic bonds. endo- or exo-mechanism of the splitting action, i.e., whether breakdown

starts from within the polymer or from the end of the polymer; and preference for pectic acid or pectin as a substrate. Both polymethylgalacturonase (PMG) and polygalacturonase (PG) cleave glycosidic bonds with the aid of water, while pectin lyase (PL) and pectate lyase (PAL) act by the transelimination mechanism. Pectin and pectate lyases are also called pectin and pectate transeliminases (PTE and PATE) (Whitaker, 1972).

2.2.3 Mechanism of Action of Pectinases

Generally there are three possible ways in which enzymatic degradation of alpha-1-4 linkages can occur in pectin: combined action of pectinesterase (PE) and polygalacturonase (PG); hydrolytic polymethylgalacturonase (PMG) reaction; and pectin transeliminase (PTE) reaction (Seegmiller and Jansen, 1952). In the process of enzyme action, there is a reduction in viscosity depending on the temperature, amount of enzyme and the type of citrus juice. Slowly the fine haze in the juice begins to agglomerate and form a floc which eventually settles out leaving the clear supernatant juice. Often, however, even the clear supernatant has some suspended material in it. Research done by Yamasaki et al. (1967), Ishii and Yokotsuka (1971, 1972, 1973) and Endo (1964) have contributed somewhat to the understanding of the mechanism of action of pectinases.

Soluble pectin was found to act as a protective colloid, and partial hydrolysis of the pectin would cause insoluble and finely divided particles to flocculate. Experiments with the haze compounds show it to be a protein-carbohydrate complex containing about 36% protein (Yamasaki et al., 1967). At a pH of 3.5, the surfaces of these protein molecules and pectin as well as other carbohydrates are negatively charged. Underneath the negative charge coat, there are positively charged proteins. Partial hydrolysis of this negative coat leads to the exposure of positively charged surfaces. In this state, the system has unlike charges attracting one another and a floc could form.

Cloud from orange juice contains mainly pectins, proteins and lipids (Baker and Bruemmer, 1969). Hesperidin has been found in the crystallized form in the orange cloud (Mizrahi and Berk, 1970). Pectinesterase is the main enzyme which determines orange cloud flocculation and the stability of the cloud seems to be a function of the ratio between the amount of flavonoid hesperidin and the molecular weight of the polymer pectin (Ben-Shalom et al., 1985).

2.2.4 Composition of Citrus Juices

In order to use a model solution which would simulate a citrus juice (especially orange juice), the composition of the juice has to be known. The composition of citrus juice has been studied by Cohen et al. (1984), Petrus and

Vandercook (1980). Cohen et al. (1984) reported an acidity content of 0.75 to 1.52 (%w/w) for Israeli orange juice as citric acid anhydrous. The second highest acid concentration was that of ascorbic acid being 35 to 70 mg vitamin C/100 ml of juice, reported by Beacham and Bonney (1937) in Florida. These workers reported the same range for all orange varieties and found no varietal differences in vitamin C levels. However, subsequent studies conducted on Florida orange juices by Nagy and Smoot (1977) showed that juices from early season (November to January, mostly Hamlin) and mid season (January to March, mostly Pineapple) contained more vitamin C than late season juices (April to July, mostly Valencia). Birdsall et al. (1961) reported that juice from California naval oranges contained about 15 mg/100 g more total vitamin C than the juice from Valencia oranges.

2.3 Modeling of pH using Reaction Equilibria in The Simulation Model Systems

2.3.1 Electrolyte Solutions and Their Modeling

The relative importance of studies of electrolyte solutions is increasing because applications to phase equilibria for chemical process design are numerous and industrially important. Process design requires applicability in a large range of concentrations, temperatures and pressures for complex systems. Maurer (1983) gave an excellent review of electrolyte solutions.

In the case of aqueous electrolytes, the solute is polar enough to allow dissociation of electrolytes. In an ideal situation, it may be assumed that a particular electrolyte completely dissociates in the liquid phase. Deviations from ideality are mostly derived from excess Gibbs energy at given temperature, pressure and composition or from the Helmholtz energy at given temperature, volume and composition for the solution of "real" species. Choice of the reference state and scale of concentration are often reviewed and depend on the suitability for specific applications (Renon, 1981; Stokes, 1979). The properties which can be derived are mainly activity coefficients, excess partial molar volumes, enthalpies, entropies and heat capacities, depending on the availability of specific data.

For calculation of the mean activity coefficients, Meissner and Kusik (1972), Bromley (1973) and Pitzer (1973) have proposed several models based on observations of experimental behavior. The most important contribution was that of Debye-Hückel who established the theoretical limiting law. Most models are based on extended Debye-Hückel equation by addition of a polynomial of ionic strength or by consideration of solvation equilibria in order to extend their applicability to higher ionic strength. Single ion activity coefficients can be calculated by the Debye-Hückel expression if the approximate effective radius of the

particular ion is given in aqueous solutions (Kielland, 1937).

2.3.2 Equilibrium Reactions in the Liquid Phase

In an electrolyte system under pressure of carbon dioxide, a number of major reactions including dissociation reactions occur in the liquid phase. Considering the composition of a citrus juice, several model juice systems can be used to simulate a citrus juice. Pure water, an aqueous solution of citric acid, an aqueous solution of ascorbic acid or a combination of all these can be used with supercritical carbon dioxide. The dissolved carbon dioxide in the solution and the presence of acids change the pH of the model systems. The significant reactions contributing to the lowering of the pH of the solution are the dissociation of ascorbic and citric acids and the formation of carbonic acid as a result of carbon dioxide being dissolved in the solution. Figures 2-1 to 2-3 show the equilibrium reactions occurring in the liquid phase of the citrus model systems considered.

2.3.3 Effect of Dissolved Carbon Dioxide on pH of Pure Water

Although the dissociation constant data of carbonic acid, produced when carbon dioxide is dissolved in water, is of great fundamental importance, from a practical point of view the true acidity expressed in terms of pH is more

Figure 2-1. Liquid-phase chemical reactions in a water-carbon dioxide binary system

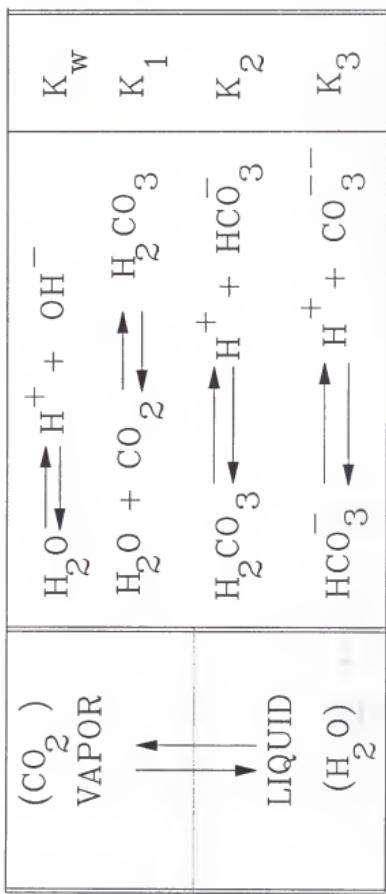


Figure 2-2. Dissociation reactions of ascorbic acid

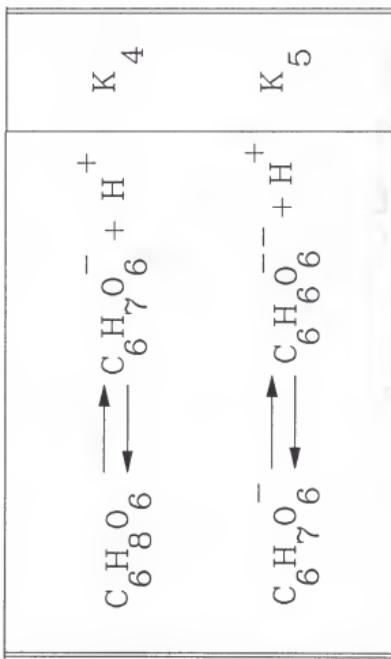
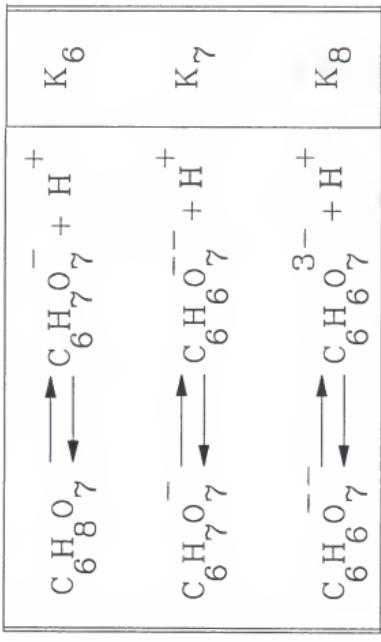


Figure 2-3. Dissociation reactions of citric acid



useful. Byke (1932) calculated the pH values for solutions of carbon dioxide in pure water. For a partial pressure of zero to 1.01×10^{-1} MPa (atmospheric pressure) of carbon dioxide. In his calculations, Byke assumed that the dissociation constant remained unchanged with process pressure. However, dissociation constant can be a function of temperature, pressure, and composition. Values for pH of solutions of carbon dioxide in water at pressures above atmospheric pressure have been determined colorimetrically by Moore and Buchanan (1930). These measurements were made in an attempt to explain the action of carbon dioxide in carbonated beverages in inhibiting the growth of bacteria. The maximum acidity of pure water was reached with a pH of 3.3 at 9.60×10^{-1} MPa when the temperature was 25°C. The conclusion was that the action of carbon dioxide solutions on bacteria was due, in part at least, to some factor other than the lowering of the solution pH (Moore and Buchanan, 1930).

In order to calculate the pH more accurately, the variations of thermodynamic properties with process pressure have to be taken into account, namely, the variations of molar volumes, equilibrium constants and activity coefficients.

2.3.4 Prediction of Thermodynamic Properties of Aqueous Electrolytes at High Pressures

2.3.4.1 Pressure dependance of molar volume

Upon addition of an electrolyte to water, short-range order among the solvent molecules is destroyed in the vicinity of the ions by local collapse of the water structure, which permits H_2O dipoles to orient in primary and more disordered secondary coordination shells about the aqueous species (Bockris, 1949; Samoilov, 1957; Duncan and Kepert, 1959). The local disruption of hydrogen bonding among the solvent dipoles by ion-solvent interaction is accompanied by a decrease in entropy as well as volume. Relatively few equations of state have been proposed that would account for the volume changes accompanying ion dissociation and ionization as a function of pressure. These equations have been reviewed by Hamman (1963) and more recently by Gancy (1972), Brummer and Gancy (1972), Helper and Wooley (1973), Olofsson and Helper (1975), and Hemmes (1972).

A general equation of state for aqueous electrolytes was described by Helgeson and Kirkham (1976) taking into account the combined effect of volume loss due to local collapse of the solvent structure (ΔV_c°) and that relating to the solvation process (ΔV_s°); that is

$$\Delta V^\circ = \Delta V_c^\circ + \Delta V_s^\circ \quad (2-3)$$

Differentiation of the above equation with respect to pressure at constant temperature leads to

$$\left(\frac{\partial \Delta V^o}{\partial P} \right)_T = -\kappa^o = -\omega N \quad (2-4)$$

where κ^o represents the standard partial molar isothermal compressibility, and ω and N are the Born parameters which can be determined experimentally knowing the partial molar Gibbs free energy of solvation for a particular ion. Using experimental data, the isothermal compressibility of an ion can be calculated from the above equation and then the change in the molar volume can be obtained by integrating the above equation from the standard pressure to the operating pressure. Partial molar compressibilities and partial molar volumes are given for a number of uni- and multivalent ions in Helgeson and Kirkham (1974a) from 1 to 5 kilobars and 25 to 500 C.

Knowing the partial molar volume of an ionic species, the change in the total reaction volume associated with the dissociation of an electrolyte can be calculated as the difference between the partial molar volumes of products minus those of reactants:

$$\Delta V^o_R = \sum v_i V^o_i \quad (2-5)$$

where ΔV^o_R = change of molar volume of reaction

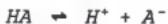
v_i = stoichiometric coefficient of species i

V_i = partial molar volume of species i

The changes of reaction volume are given for a number of weak acids in Owen and Brinkley (1941), Disteche (1965), Hamann (1957), Redlich and Bigeleisen (1942), Harned and Owen (1958) and Bodansky and Kauzmann (1962).

2.3.4.2 Pressure dependence of equilibrium constant

For the following general dissociation reaction of an acid, the dissociation equilibrium is characterized by the dissociation constant, K:



The dissociation constant (also referred to as the equilibrium constant) is the quotient of the activities, a_i , of the chemical species involved in the reaction. The activity is a measure of the chemical potential of a particular substance and can be expressed as the product of

the molar concentration and the corresponding activity coefficient:

$$K_n = \prod_i a_i = \frac{a_{H^+} a_{A^-}}{a_{HA}} = \frac{x_{H^+} x_{A^-}}{x_{HA}} \cdot \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} \quad (2-6)$$

where K_n = equilibrium constant of reaction n

a_i = activity of species i

x_i = molar concentration of species i

γ_i = activity coefficient of species i

The equilibrium constant is a function of temperature, pressure and composition. Although the equilibrium constants for a number of dissociation reactions are available at mostly the standard conditions of 25°C and atmospheric pressure, little or no data are available at other temperatures and at higher pressures. It is therefore necessary to develop methods of determining the temperature and pressure dependence of the equilibrium constant using the available thermodynamic data together with thermodynamic formulas.

The following equation is the mathematical expression of the Le Chatelier's principle, stating the pressure dependence of the equilibrium constant at constant

temperature(T) and constant composition(x), (Suzuki and Taniguchi, 1972):

$$\left[\frac{\partial \ln K}{\partial P} \right]_{x,T} = \frac{-\Delta V_R}{RT} \quad (2-7)$$

where K = equilibrium constant

R = ideal gas constant

P = pressure

T = temperature

ΔV = change of reaction volume

2.3.4.3 Pressure dependence of activity coefficient

Knowing or calculating the mean activity coefficients of the ionic or molecular species involved in the dissociation reactions at standard conditions, the activity coefficient can be estimated at higher pressures at constant temperature and composition by the following relation derived from Gibbs-Duhem expression (Disteche, 1972):

$$\left(\frac{\partial \log \gamma}{\partial P} \right)_{x, T} = \frac{\Delta V}{RT} \quad (2-8)$$

where γ =activity coefficient

P = pressure

ΔV = change in the partial molar volume of the ion

R = ideal gas constant

T = temperature

x = composition.

The pH of an electrolyte solution is related to the activity of hydrogen ions in the solution. The equilibrium concentrations of ions and other chemical species can be calculated through expressions that relate concentration to the thermodynamic parameters such as the equilibrium constant, the compressibility coefficient, the molar volume and the activity coefficient. The values of these parameters at higher temperatures and pressures can be estimated by using data at standard conditions given in the literature along with the appropriate thermodynamic relation. The next chapter discusses the procedure used to calculate the equilibrium concentrations and subsequently the pH of the electrolyte solutions used as the citrus simulation systems in this study.

CHAPTER 3 MATERIALS AND METHODS

This chapter gives the procedure for developing the thermodynamic models for the four simulation systems of pure water-carbon dioxide, ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide and ascorbic acid-citric acid-water-carbon dioxide. In developing the pH model, the model parameters such as the activity coefficients and the equilibrium constants were first calculated and later used in a series of algebraic equations to calculate the equilibrium concentrations of the chemical species involved in the solutions. The pH of the simulation solutions were later calculated from the equilibrium concentration of hydrogen ions. Once the pH values were calculated for every simulation system at various process conditions, they were compared with actual experimental pH values for all four systems as well as for single strength orange juice.

3.1 Development of the Thermodynamic Models

3.1.1 Calculation of Activity Coefficients

3.1.1.1 Pierotti et al. method for carbonic acid

The activity coefficient of the carbonic acid in the mathematical model was calculated using the modified

equation of Pierotti et al. (1959). This equation relates the infinite dilution activity coefficients to the molecular structures of the solute and solvent molecules through the number of carbon atoms for both species as shown in equation (3-1).

$$\log \gamma_1 = A_{1,2} + B_2 \frac{N_1}{N_2} + \frac{C_1}{N_1} + D(N_1 - N_2)^2 + \frac{F_2}{N_2} \quad (3-1)$$

where subscript 1 refers to solute and 2 to solvent and

γ_1 = activity coefficient of solute (carbonic acid)

$A_{1,2}$ = coefficient which depends on nature of solute
and solvent functional groups

B_2 = coefficient which depends only on nature of
solvent functional groups

C_1 = coefficient which depends only on solute
functional groups

D = coefficient independent of solute and solvent
functional groups

F_2 = coefficient which essentially depends on nature
of solvent functional groups

N_1, N_2 = number of carbon atoms in solute and solvent,
respectively.

The numerical values for the parameters in equation (3-1) were taken from Pierotti et al. (1959) parameter table which has been developed for a number of organic acids and solvents. Table 3-1 gives the parameter values for the calculation of the activity coefficient of carbonic acid in water.

Table 3-1. Pierotti parameters for calculating the infinite dilution activity of carbonic acid in water.

$A_{1,2}$	-1.00
B_2	0.662
C_1	0.490
D	0.0
F_2	0.0
N_1	1.0
N_2	0.0

3.1.1.2 Debye-Hückel method for individual ions

Activity coefficients for the single ions in the solution were calculated using an extended Debye-Hückel equation (Pitzer, 1973). The equation is based on the interionic attraction effects of the aqueous solution, expressed as the ionic strength, μ , of the solution.

Equation (3-2) holds for the range of ionic strengths ($0 < \mu < 0.7$):

$$-\log \gamma_i = \frac{0.512 Z_A Z_B \sqrt{\mu}}{1 + a B \sqrt{\mu}} \quad (3-2)$$

where a = diameter of ion in Angstrom (A)

B = a term depending on temperature and dielectric constant of the solvent

Z_i = ionic charge of species i

μ = ionic strength of solution

The approximate values for the effective ionic radii of inorganic and organic ions are given in the following table (Kielland, 1937):

Table 3-2. Approximate effective ionic radii of Inorganic and organic ions

Ion Species	Approximate Ionic Radii (Angstroms)
H^+	9.0
OH^-	3.5
HCO_3^-	9.0
CO_3^{--}	3.5
$HAsc^-$	3.5
Asc^{--}	3.5
H_2Cit^-	3.5
$HCit^{--}$	4.5
Cit^{---}	5.0

3.1.1.3 UNIFAC method for ascorbic and citric acids

The UNIFAC (UNIQUAC Functional Group Activity Coefficients) method was used to estimate the activity coefficients of ascorbic and citric acids. This method is a group contribution method that uses existing phase equilibrium data and applies them to the structural groups of various compounds. In the UNIFAC method the logarithm of the activity coefficient is estimated to be the sum of two contributions: a combinatorial part, essentially due to differences in size and shape of the molecule in the mixture, and a residual part, essentially due to energy interactions as shown in equation (3-3):

$$\ln(\gamma_i) = \ln(\gamma_i^c) + \ln(\gamma_i^r) \quad (3-3)$$

where γ_i^c = combinatorial activity coefficient

γ_i^r = residual activity coefficient

The combinatorial part of the above equation was calculated using equations (3-4) to (3-9) from Magnussen et al. (1981):

$$\ln \gamma_1^c = \ln \frac{\phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1} + l_1 - \frac{\phi_1}{x_1} (x_1 l_1 + x_2 l_2) \quad (3-4)$$

and

$$\ln \gamma_2^c = \ln \frac{\phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2} + l_2 - \frac{\phi_2}{x_2} (x_1 l_1 + x_2 l_2) \quad (3-5)$$

where

$$\begin{aligned} \phi_1 &= \frac{x_1 x_1}{x_1 x_1 + x_2 x_2} \\ \theta_1 &= \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \end{aligned} \quad (3-6a, b)$$

and

$$\begin{aligned} \phi_2 &= \frac{x_2 x_2}{x_1 x_1 + x_2 x_2} \\ \theta_2 &= \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \end{aligned} \quad (3-7a, b)$$

(Noting that $\phi_1 + \phi_2 = 1$ and $\theta_1 + \theta_2 = 1$.)

$$I_1 = \frac{Z}{2} (x_1 - q_1) - (x_1 - 1) \quad ; \quad Z = 10 \quad (3-8a, b)$$

$$I_2 = \frac{Z}{2} (x_2 - q_2) - (x_2 - 1)$$

$$x_1 = \sum v_k^{(1)} R_k \quad ; \quad x_2 = \sum v_k^{(2)} R_k \quad (3-9a, b)$$

$$q_1 = \sum v_k^{(1)} Q_k \quad ; \quad q_2 = \sum v_k^{(2)} Q_k$$

where x_1, x_2 = mole fraction of component 1 and 2
 v = number of groups in molecule 1 or 2
 R_k = the van der Waals volume for group k
 Q_k = the van der Waals surface area for group k
 k = group number (assigned) from table of
group volumes and surface areas (Table 3-3).

The group volumes and surface areas for the combinatorial activity coefficients were taken from the UNIFAC tables of vapor-liquid equilibrium data by Magnussen et al. (1981) and are given in Table 3-3.

Table 3-3. Group volume and surface-area parameters for citric and ascorbic acids used in the UNIFAC method

Acid/Parameter	k	R _k	Q _k
Citric(-COOH)	43	1.3013	1.200
Citric(-CH ₂)	2	0.6744	0.540
Citric(-C-)	15	1.000	1.200
Citric(-C-)	4	0.2195	0
Ascorbic(-OH)	15	1.000	1.200
Ascorbic (-C=C-)	9	0.6605	0.485
Ascorbic(-C-H)	3	0.4469	0.228
Ascorbic (-CCOO-)	23	1.6764	1.420

The residual part of the equation for calculating the activity coefficients of ascorbic and citric acids was calculated using equations (3-10) to (3-12):

$$\ln \gamma_1^R = \sum v_k^{(1)} [\ln \Gamma_k - \ln \Gamma_k^{(1)}] \quad (3-10a, b)$$

$$\ln \gamma_2^R = \sum v_k^{(2)} [\ln \Gamma_k - \ln \Gamma_k^{(2)}]$$

where

$$\ln \Gamma_k = Q_k [1 - \ln (\sum \theta_m \psi_{mk}) - \sum (\theta_m \psi_{km} / \sum \theta_n \psi_{nm})] \quad (3-11)$$

and m and n=1,2,...,N(all groups)

$$\theta_m = \frac{Q_m X_m}{\sum Q_n X_n} \quad ; \quad X_m = \frac{\sum v_m^{(j)} x_j}{\sum \sum v_m^{(j)} x_j} \quad (3-12)$$

j=1,2,...,M; n=1,2,...,N, Also,

j = component number (1 or 2 for a binary mixture)

M = total number of components (=2 for a binary mixture)

n = group number

N = total groups

θ_m = group surface area fraction

X_m = group fraction (For example, for a equimolar mixture of butane and hexane, the group fractions for CH_3 and CH_2 are 4/10 and 6/10, respectively.)

x_j = mole fraction of molecule j in the mixture

$v_m^{(j)}$ = number of groups of type m in molecule j

ψ_{rm} = $\exp(-a_{rm}/T)$

T = temperature (K)

The parameter a_{nm} is a group interaction parameter which is a measure of the difference in interaction energy between groups n and m given in Magnussen et al. (1981).

The solubility of carbon dioxide in the solution at the process temperature and pressure was approximated using vapor-liquid equilibrium data for carbon dioxide and water. Solubility values for carbon dioxide has been published by Wiebe and Gaddy (1940) for the $\text{CO}_2\text{-H}_2\text{O}$ binary system between 12 and 100°C and at pressures from 2.53 to 70.70 MPa. The solubility of carbon dioxide at atmospheric pressure was calculated using equation (3-13), (Wiebe and Gaddy, 1940):

$$R \ln S = A + B/T + C \ln T + D T \quad (3-13)$$

where S=mole fraction solubility of carbon dioxide in pure water at one atmosphere (1.0136×10^3 KPa)

$$A = -1330.03 \text{ J/(K.mole)}$$

$$B = 7.2733 \text{ KJ/mole}$$

$$C = 180.295 \text{ J/(K.mole)}$$

$$D = -0.009174 \text{ J/(K}^2\text{.mole)}$$

$$R = 8.31957 \text{ J/(K.mole)}$$

$$T = \text{absolute temperature (273 K} < T < 353 \text{ K)}$$

An interpolation program was written to calculate the solubility at the exact temperature and pressure of the supercritical process. The parameters of the thermodynamic model were either taken from data available in thermodynamic literature or calculated using the reaction equilibria formulae. These parameters included the equilibrium constants, k , the molecular and single ion activity coefficients, γ , compressibility coefficients, κ , and changes of reaction volumes, ΔV .

3.1.2 Calculation of pH of the Simulation Systems

The pH of the model solutions was calculated using equation (3-14) expressing the pH as the negative logarithm of the activity of the hydrogen ions:

$$pH = -\log a_{H^+} = -\log x_{H^+} - \log \gamma_{H^+} \quad (3-14)$$

where a_{H^+} =activity of hydrogen ions

x_{H^+} =concentration of hydrogen ions

γ_{H^+} =activity coefficient of hydrogen ions.

3.1.3 Systematic Method for Calculating Equilibrium Concentrations

A systematic method was used to determine the equilibrium concentrations of the unknown species in the model solution. The first step is to define a set of equations for all the reactions that appear to have a major effect on the concentration of hydrogen ions. These equations included expressions for the equilibrium constant in the major equilibria for the particular model system, the mass-balance equation, and the charge-balance equation. Mass balance equations were algebraic expressions relating the equilibrium concentrations of the various species to one another and to the analytical concentrations of the substances present in the solution. The charge-balance equation expresses the relationship that the concentrations of the cations and anions must be such that the solution is electrically neutral. All of these expressions will result in a number of independent equations which will be equal to the number of unknown concentrations.

3.1.3.1 Ionization constant of water

Marshall and Frank (1981) gave the ion product of water for a range of temperatures, shown in Table 3-4:

Table 3-4. Ionization constant for water (K_w)

$-\log K_w$	Temperature, $^{\circ}\text{C}$	$-\log K_w$	Temperature, $^{\circ}\text{C}$
14.9435	0	13.8330	30
14.7338	5	13.6801	35
14.5346	10	13.5348	40
14.3463	15	13.3960	45
14.1669	20	13.2617	50
14.0000	24	13.1396	55
13.9965	25	13.0171	60

3.1.3.2 Numerical values of equilibrium constants

The equilibrium (dissociation) constants of all of the reactions involved in the model solutions were found in the literature and are given in Table 3-5 (Meites, 1963):

Table 3-5. Dissociation constants for carbonic, ascorbic and citric acids

Acid	Dissociation Constant
Carbonic(HCO_3^-)	$K_1=5.61 \times 10^{-11}$
Carbonic(H_2CO_3 to CO_3^{--})	$K_2=4.31 \times 10^{-7}$
Carbonic(H_2CO_3 to CO_2)	$K_3=4.42 \times 10^{-7}$
Ascorbic($\text{C}_6\text{H}_8\text{O}_6$)	$K_4=7.94 \times 10^{-5}$
Ascorbic($\text{C}_6\text{H}_7\text{O}_6^-$)	$K_5=1.62 \times 10^{-12}$
Citric($\text{C}_6\text{H}_8\text{O}_7$)	$K_6=7.45 \times 10^{-4}$
Citric($\text{C}_6\text{H}_7\text{O}_7^-$)	$K_7=1.73 \times 10^{-5}$
Citric($\text{C}_6\text{H}_6\text{O}_7^{--}$)	$K_8=4.02 \times 10^{-7}$

3.1.3.3 Set of equations for the pure water-carbon dioxide system

The chemical reactions involved in the binary solution of pure water and carbon dioxide involved the dissociation of water and the three dissociation reactions of the carbonic acid. These four equations were derived using the expressions for the equilibrium constants shown in equations (3-15a) to (3-15d) :

$$K_w = \frac{a_{H^+} \cdot a_{OH^-}}{a_{H_2O}} \quad (3-15a)$$

$$K_1 = \frac{a_{CO_3^{2-}} \cdot a_{H^+}}{a_{HCO_3^-}} \quad (3-15b)$$

$$K_2 = \frac{a_{HCO_3^-} \cdot a_{H^+}}{a_{H_2CO_3}} \quad (3-15c)$$

$$K_3 = \frac{a_{H_2O} \cdot a_{CO_2}}{a_{H_2CO_3}} \quad (3-15d)$$

In the above equations, the activities can be written as products of molar concentrations and activity coefficients, as shown in equations (3-16a) to (3-16d):

$$(\gamma_{H^+} \cdot \gamma_{OH^-}) x_{H^+} x_{OH^-} - K_w = 0 \quad (3-16a)$$

$$(\gamma_{H^+} \cdot \gamma_{CO_3^{2-}}) x_{H^+} x_{CO_3^{2-}} - (\gamma_{HCO_3^-} \cdot K_1) x_{HCO_3^-} = 0 \quad (3-16b)$$

$$(\gamma_{H^+} \cdot \gamma_{HCO_3^-}) x_{H^+} x_{HCO_3^-} - (\gamma_{H_2CO_3} \cdot K_2) x_{H_2CO_3} = 0 \quad (3-16c)$$

$$(\gamma_{CO_2}) x_{CO_2} - (\gamma_{H_2CO_3} \cdot K_3) x_{H_2CO_3} = 0 \quad (3-16d)$$

The two other equations that relate the concentrations of different species in the solution together are the mass balance and the charge balance equations (3-17) and (3-18):

Carbon mass balance equation:

$$x_{CO_2} + x_{H_2CO_3} + x_{HCO_3^-} + x_{CO_3^{2-}} - S_{CO_2} = 0 \quad (3-17)$$

Charge balance (electroneutrality) equation:

$$x_{H^+} - x_{OH^-} - x_{HCO_3^-} - 2x_{CO_3^{2-}} = 0 \quad (3-18)$$

3.1.3.4 Set of equations for the ascorbic acid-water-carbon dioxide system

In addition to the equilibrium constant equations in the pure water-carbon dioxide system, two more equations can be written for the Ascorbic acid-water-carbon dioxide system which take into account the dissociation reactions of ascorbic acid. The equations for charge and mass balances have to be modified because of additional ions present in the solution. The equilibrium constant equations are given below:

$$K_4 = \frac{a_{H^+} \cdot a_{C_6H_7O_6^-}}{a_{C_6H_6O_6}} \quad (3-19)$$

$$K_5 = \frac{a_{H^+} \cdot a_{C_6H_6O_6^{2-}}}{a_{C_6H_7O_6^-}} \quad (3-20)$$

Substituting the activities with the product of molar concentrations and the activity coefficients, equations (3-21) and (3-22) were obtained:

$$(\gamma_{H^+} \cdot \gamma_{C_6H_7O_6^-}) X_{H^+} \cdot X_{C_6H_7O_6^-} - K_4 \gamma_{C_6H_6O_6} \cdot X_{C_6H_6O_6} = 0 \quad (3-21)$$

$$(\gamma_{H^+} \cdot \gamma_{C_6H_6O_6^{2-}}) \cdot x_{H^+} \cdot x_{C_6H_6O_6^{2-}} - K_5 \cdot \gamma_{C_6H_7O_6^-} \cdot x_{C_6H_7O_6^-} = 0 \quad (3-22)$$

The mass balance equation (3-23):

$$x_{CO_2} + x_{H_2CO_3} + x_{HCO_3^-} + x_{CO_3^{2-}} - 6x_{C_6H_6O_6} \\ + 6x_{C_6H_7O_6^-} + 6x_{C_6H_5O_6^{2-}} - S_{CO_2} = 0 \quad (3-23)$$

The charge balance equation (3-24):

$$x_{H^+} - x_{OH^-} - x_{HCO_3^-} - x_{C_6H_7O_6^-} - 2x_{C_6H_6O_6^{2-}} - 2x_{CO_3^{2-}} = 0 \quad (3-24)$$

3.1.3.5 Set of equations for the citric acid-water-carbon dioxide system

In this ternary system, there will be three other equilibrium constant equations, as well as, different mass and charge-balance equations due to new chemical species in the model solution:

Equilibrium constant equations (3-25) to (3-27):

$$K_6 = \frac{a_{H^+} \cdot a_{C_6H_5O_7^-}}{a_{C_6H_6O_7^2}} \quad (3-25)$$

$$K_7 = \frac{a_{H^+} \cdot a_{C_6H_6O_7^{2-}}}{a_{C_6H_5O_7^-}} \quad (3-26)$$

$$K_8 = \frac{a_{H^+} \cdot a_{C_6H_5O_7^{3-}}}{a_{C_6H_6O_7^{2-}}} \quad (3-27)$$

By substituting the activities with molar concentrations and the activity coefficients, expressions (3-28) to (3-30) were obtained:

$$(\gamma_{C_6H_5O_7^-} \cdot \gamma_{H^+}) x_{H^+} \cdot x_{C_6H_5O_7^-} - K_6 \cdot \gamma_{C_6H_6O_7^2} \cdot x_{C_6H_6O_7^2} = 0 \quad (3-28)$$

$$(\gamma_{C_6H_6O_7^{2-}} \cdot \gamma_{H^+}) X_{H^+} \cdot X_{C_6H_6O_7^{2-}} - K_7 \cdot \gamma_{C_6H_7O_7^-} \cdot X_{C_6H_7O_7^-} = 0 \quad (3-29)$$

$$(\gamma_{C_6H_5O_7^{2-}} \cdot \gamma_{H^+}) X_{C_6H_5O_7^{2-}} \cdot X_{H^+} - K_8 \cdot \gamma_{C_6H_6O_7^{2-}} \cdot X_{C_6H_6O_7^{2-}} = 0 \quad (3-30)$$

The mass-balance equation (3-31):

$$X_{CO_2} + X_{H_2CO_3} + X_{HCO_3^-} + X_{CO_3^{2-}} - 6X_{C_6H_6O_7^-} + 6X_{C_6H_7O_7^-} + 6X_{C_6H_5O_7^{2-}} + 6X_{C_6H_6O_7^{2-}} - S_{CO_2} = 0 \quad (3-31)$$

The charge-balance equation (3-32):

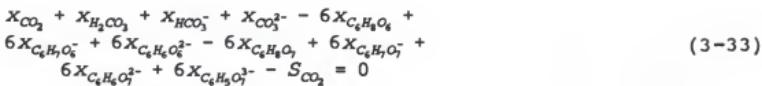
$$X_{H^+} - X_{OH^-} - X_{HCO_3^-} - X_{C_6H_7O_7^-} - 2X_{C_6H_6O_7^{2-}} - 3X_{C_6H_5O_7^{2-}} - 2X_{CO_3^{2-}} = 0 \quad (3-32)$$

3.1.3.6 Set of equations for the ascorbic acid-citric acid-water-carbon dioxide system

The set of equations resulting from the equilibrium expressions for the three previous simulation systems were all used in developing the pH model for the quaternary system of ascorbic acid-citric acid-water-carbon dioxide. However, the mass balance and charge balance equations would be different

since both ascorbic acid and citric acid are present in the solution:

The mass balance equation (3-33):



The charge-balance equation (3-34):



In developing the thermodynamic models, the set of equations resulting from the expressions for dissociation constants and mass and charge balances were solved simultaneously for the activity of hydrogen ions (H^+) using the Newton-Raphson iteration method. The molar concentrations of all the ionic and non-ionic species in the solution made up a matrix of eleven elements. By assigning initial concentration values and inverting the coefficient matrix, the iterated concentrations

converged to a set of new values corresponding to the equilibrium concentrations in the solution. A FORTRAN program was written to do the iteration procedure and calculate the concentration of the hydrogen ions at the process temperature and pressure. A listing of this program is given in the Appendix.

3.2 Experimental

A series of experiments were performed under different process conditions with different levels of acid concentration to compare the pH values predicted by the mathematical models to the actual pH of the solution. The pH values were measured at high pressures, and for this purpose a specially designed pH probe was used which could withstand high pressures.

3.2.1 High Pressure pH Probe

The activity of hydrogen ions in the simulation solutions was measured with a pH measuring system consisting of a glass electrode, a reference electrode, and a pH meter. The reading on the pH meter is the glass electrode potential which is proportional to the hydrogen ion activity corrected by the reference electrode potential. The major components of the glass electrode are the pH-sensitive glass bulb, the probe shell, and the filling solution. The glass bulb is a membrane which shows an electric potential when it comes in contact with hydrogen ions. Ordinary pH probes have very limited

pressure ranges and can not be used for measurements at high pressures. At high pressures the glass bulb and the probe casing have to be made of resistant polymeric material to avoid destruction of the probe, since the internal pressure of the probe would be lower than the external pressure and this leads to the collapse of the probe casing. The high pressure pH probe used in the experiments was a Markson (Phoenix, AZ.) with a gel filled combination Ag/AgCl electrode, a Teflon reference junction, and a stainless steel bulkhead fitting. This special probe was originally designed for taking pH measurements at deep places of oceans where the probe will be under high pressures. The pH meter was an Orion EA 920 (Cambridge, MA.).

3.2.2 Experimental Design

The experimental design chosen to determine the combinations of model variables was the Box and Behnken(1960) design. In this design, a fraction of the three-level factorial arrangements was used. The levels of each of the quantitative factors were assumed equally spaced and they were coded -1, 0, and 1. The most commonly used coding scheme was used to define the coded variables, x_i , which were defined in standardized form as shown in equation (3-35):

$$x_{ui} = \frac{X_{ui} - X_{i,m}}{S_i} \quad ; \quad i=1, 2, \dots, k \quad (3-35)$$

where $X_{i,m}$ is the mean of the X_{ui} values ($u=1,2,\dots,N$) and S_i is the scale factor.

The coded variables were applied to the experimental variables which included six levels of process pressure and three levels of concentration for ascorbic and citric acids each and for every simulation system.

3.2.3 Preliminary Experiments

A set of preliminary experiments were performed to determine the effect of sugar (sucrose) on the solubility of carbon dioxide and the subsequent change in pH of the solution. Other experiments were performed to determine the effect of process temperature on the pH of the model solutions. The sucrose concentrations were at 0 and 20%, and the process temperatures were 32, 37, and 42°C. These experiments were performed for six levels of process pressure, namely, 0, 0.690, 1.379, 2.758, 4.137, 5.861 MPa.

3.2.4 Experiments on the Effect of Pressure and Acid Concentrations on the pH of Model Solutions

To confirm the pH values predicted by the thermodynamic model, a set of experiments were performed with a solution of citric acid (certified A.C.S. reagent, Registry No. 876435 provided by Fischer Scientific) and ascorbic acid (certified A.C.S. Reagent, Registry No. 03912LX provided by Aldrich Chemical Company, Inc., Milwaukee, Wisconsin) to simulate citrus juice. The concentration levels of the two acids and

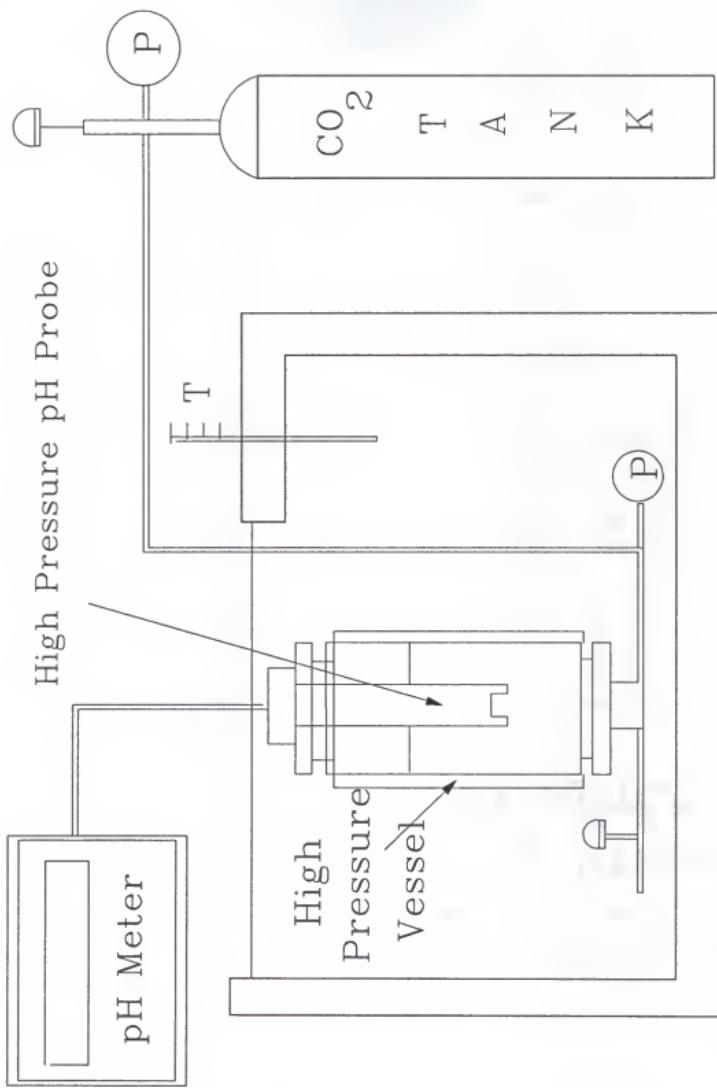
process temperature and pressure were varied according to the Box-Behnken design(1960). Table 3-6 shows the design variables and their levels in the experiments. Concentration of citric acid varied from 0 to 1.17 grams per liter of solution and that for ascorbic acid was from 0 to 19.5 grams per liter of solution. Process pressure ranged from 0 to 34.48 MPa.

Table 3-6. Coded design variable settings for the pH experiments

Pressure, atm.	Citric Acid Concentration, g/L	Ascorbic Acid Concentration, g/L
+1	+1	0
+1	-1	0
-1	+1	0
-1	+1	0
+1	0	+1
+1	0	-1
-1	0	-1
-1	0	-1
0	+1	+1
0	-1	+1
0	-1	-1
0	0	0

In the experiments with pure water, a solution of pH adjuster(pHIX Adjuster provided by Orion Research Inc., Cambridge, MA.) was used to stabilize the pH readings, since the concentration of electrolytes in the solution would be low. A high pressure vessel was used as a closed system in the high pressure experiments, and the pH was monitored by the Orion pH meter during the process. Experiments were conducted in a constant-temperature water bath (Blue M, Blue Island, IL.). Equilibration time was a minimum of 2 hours, determined in the preliminary experiments. Figure 3-1 shows the schematic of the experimental set-up for measuring the pH in the supercritical vessel. To take the pH measurements, 40 ml of solution was put into the stainless steel pressure vessel and then the pH electrode, previously fixed to the lid of the vessel, would fit into the head of the vessel. The rubber O-rings on the lid prevented any leaks from the pressure vessel and before each run the whole system including pressure valves, pressure hoses and the pressure vessel were purged of air by CO₂ gas to minimize the oxidation of the acid solutions. The pressure of the vessel was regulated by a sensitive pressure valve and read on a pressure gage. Temperature inside the vessel was maintained by the water bath and the readings were taken by a mercury thermometer as well as the pH meter thermocouple. The pH electrode was kept in an Orion storage solution to prevent drying and calibrated by standard buffer solutions before each experiment. Once the

Figure 3-1. Schematic of the experimental setup for measuring pH in the supercritical vessel at high pressures



Temperature-Controlled Water Bath with Agitation

solution was placed in the pressure vessel and subsequently into the water bath, 15 minutes was allowed to pass for the solution to come to the same temperature as the water bath before pressurization.

3.3 Statistical and Sensitivity Analyses

The pH values obtained from the experiments with the effect of sugar concentration and process temperature, were compared using a t-test statistics with a 0.5% level of significance. The null hypothesis was that the difference of mean pH values for each set of treatments was not different ($d = \mu_1 - \mu_2 = 0$). The test statistic was determined using equation (3-36):

$$t = \frac{d_{avg} - \mu_d}{s_d / \sqrt{n}} \quad (3-36)$$

where d_{avg} = average difference of pH values of the two treatments

μ_d = $\mu_1 - \mu_2$ = difference between mean pH values

s_d = standard deviation of paired differences

n = number of paired samples

The correlation coefficients for the pH models were calculated using the following relation (3-37):

$$r = \sqrt{\frac{\sum (\hat{pH} - \bar{pH})^2}{\sum (pH - \bar{pH})^2}} \quad (3-37)$$

where r = coefficient of correlation

$\sum (\hat{pH} - \bar{pH})^2$ = regression sum of squares

$\sum (pH - \bar{pH})^2$ = total sum of squares

\bar{pH} = mean pH value

\hat{pH} = estimated pH value

pH = measured pH value

Since the parameters of the pH models developed for the four simulation systems were either calculated or taken from the literature, and some assumptions were made in estimating them, their effect on the predicted pH values were studied. The calculated activity coefficients and equilibrium constants used in the pH model were decreased or increased by a factor of 10% to determine how sensitive the model is to variation of these parameters. Also, the effects of carbon dioxide solubility values as well as the influence of the concentrations of ascorbic and citric acid on the accuracy of the pH models were also studied.

CHAPTER 4 RESULTS AND DISCUSSION

For the four simulation systems of pure water-carbon dioxide, ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide, and ascorbic acid-citric acid-water-carbon dioxide, the activity coefficients and the equilibrium constants were first calculated and later used in the iteration program to calculate the pH. Whenever there were available thermodynamic data, the variations of the activity coefficients and the equilibrium constants with pressure were also calculated. The values of pH calculated by the thermodynamic model were later compared with the pH values measured experimentally for each simulation model.

4.1 Pure Water-Carbon Dioxide Simulation System

4.1.1 Calculated Activity Coefficients

The activity coefficients for the ions and other chemical species in the water-carbon dioxide binary system were calculated using the methods discussed in the previous chapter and are given in Table 4-1 with the corresponding method of calculation.

4.1.2 Variation of Activity Coefficients with Pressure

Equation 2-4 in chapter 2 relates compressibility coefficient to change in partial molar volume as pressure is increased at a constant temperature. By integrating equation 2-4 with respect to pressure and using the data given in the literature for compressibility coefficients and partial molar volumes at standard conditions, the change in molar volume was calculated. Assuming compressibility coefficients stay constant with temperature and pressure, the partial molar volume of the ions would be:

$$V_i = 10^{\log V_i^{\circ} + \frac{k_T P_o - k_T P}{2.303}} \quad (4-1)$$

where V_i =partial molar volume of species i at pressure P
and temperature T

V_i° =partial molar volume of species i at standard
pressure

(101.36 KPa) and temperature (25° C)

k_T =isothermal compressibility coefficient

P_o =standard pressure

P =process pressure

The change in the molar volume of the ions with respect to process pressure ($\Delta P = P - P_0$) would then be $\Delta V_i = V_i^o - V_i$

Table 4-2 gives the values of the isothermal compressibility coefficients for the four ions present in the water-carbon dioxide system.

Since these values for the compressibility coefficients were given in $\text{cm}^3/\text{mole.KPa}$, integration of equation 2-4 without the pressure term in the denominator would result in the following equation:

$$V_i = V_i^o + k_T P_0 - k_T P \quad (4-2)$$

Using the data given in Table 4-2, the change of molar volume with process pressure for the four ions in the solution are given in the following equations:

$$\Delta V_{H^+} = 0 \text{ (cm}^3/\text{mole)} \quad (4-3a)$$

$$\Delta V_{OH^-} = -2.9 \times 10^{-4} P + 5.0 \times 10^{-2} \text{ (cm}^3/\text{mole)} \quad (4-3b)$$

$$\Delta V_{HCO_3^-} = -4.0 \times 10^{-5} P + 8.0 \times 10^{-3} \text{ (cm}^3/\text{mole)} \quad (4-3c)$$

Table 4-1. Calculated activity coefficients for water-carbon dioxide system

Chemical Species	Calculated Activity Coefficient, γ	Method of Calculation
H^+	0.830	Debye-Hückel
OH^-	0.760	Debye-Hückel
CO_3^{--}	0.360	Debye-Hückel
HCO_3^-	0.775	Debye-Hückel
H_2CO_3	0.412	Pierotti et al.

Table 4-2. Compressibility coefficients of the ions in the water-carbon dioxide system

Ionic Species	Isothermal Compressibility Coefficient, k_T (cm ³ /mole.KPa)
H^+	0
OH^-	-2.94×10^{-1}
HCO_3^-	-4.05×10^{-2}
CO_3^{--}	-7.60×10^{-1}

(Source: Helgeson and Kirkham, 1976)

$$\Delta V_{CO_3^{2-}} = -7.5 \times 10^{-4}P + 7.5 \times 10^{-3} \quad (cm^3/mole) \quad (4-3d)$$

The change of molar volume for carbonic acid ($\Delta V_{H_2CO_3}$) is given by Disteche (1975) to be $-27.0 \text{ cm}^3/\text{mole}$ at standard conditions. Using the above equations and the change of molar volume for carbonic acid, the variations in the activity coefficients with pressure in the water-carbon dioxide system were formulated using equation 2-8 and are given below:

$$\log \gamma_{H^+} = -9.69 \times 10^{-2} \quad (4-4a)$$

$$\log \gamma_{OH^-} = -1.193 \times 10^{-1} + 1.030 \times 10^{-5}P - 2.575 \times 10^{-8}P^2 \quad (4-4b)$$

$$\log \gamma_{CO_2} = -9.69 \times 10^{-2} \quad (4-4c)$$

$$\log \gamma_{H_2CO_3} = -3.774 \times 10^{-1} - 4.79 \times 10^{-5}P \quad (4-4d)$$

$$\log \gamma_{HCO_3^-} = -1.107 \times 10^{-1} + 1.421 \times 10^{-6}P - 3.550 \times 10^{-9}P^2 \quad (4-4e)$$

$$\log \gamma_{CO_3^{2-}} = -4.436 \times 10^{-1} + 1.332 \times 10^{-6}P - 6.661 \times 10^{-9}P^2 \quad (4-4f)$$

4.1.3 Variation of Equilibrium Constants with Pressure

The change in the reaction volume for the four main equilibrium reactions in the water-carbon dioxide system were found in the literature and are given below: (Meites, 1963; Disteche, 1972)

$$\Delta V_{K_w} = -20.3 \text{ cm}^3/\text{mole}$$

$$\Delta V_{K_1} = -27.0 \text{ cm}^3/\text{mole}$$

$$\Delta V_{K_2} = -29.0 \text{ cm}^3/\text{mole}$$

$$\Delta V_{K_3} = -27.8 \text{ cm}^3/\text{mole}$$

Using the above data for the change in reaction volume together with equation 2-7, the following expressions were obtained for the equilibrium constants as a function of process pressure. Equation 2-7 was integrated with respect to pressure at constant temperature:

$$\log K_w = -13.677 + 3.6 \times 10^{-5} P \quad (4-5a)$$

$$\log K_1 = -10.252 + 5.0 \times 10^{-5} P \quad (4-5b)$$

$$\log K_2 = -6.366 + 5.0 \times 10^{-5} P \quad (4-5c)$$

$$\log K_3 = -6.355 + 4.8 \times 10^{-5} P \quad (4-5d)$$

The above expressions for activity coefficients and equilibrium constants as functions of pressure were substituted in the set of simultaneous equations for the water-carbon dioxide system given in chapter 3. Solution of these equations by the Newton-Raphson iteration method gave the equilibrium concentration for the hydrogen ions in the solution from which the pH of the system was calculated.

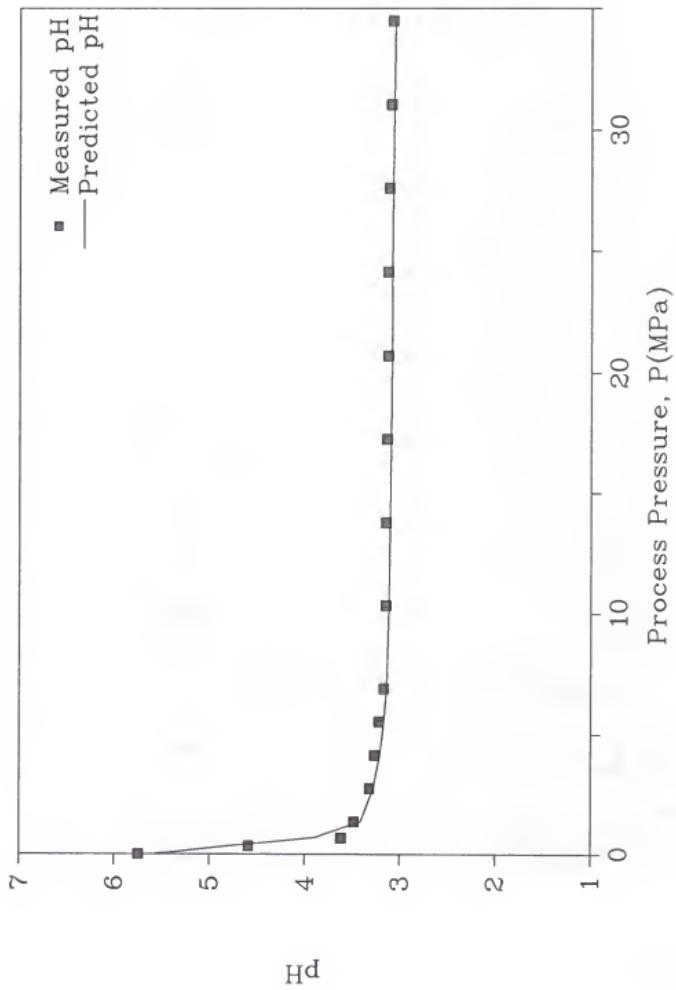
4.1.4 Comparison of the Experimental and Calculated pH values

4.1.4.1 Effect of extreme process pressures

The pH values up to a pressure of 34.48 MPa predicted by the mathematical model are compared with the experimental pH values measured by the high pressure probe in Table A-1 (in Appendix A). Figure 4-1 is the plot of the predicted and measured pH values at different process pressures. As indicated by this plot, the measured pH values are closely predicted by the pH values calculated by the mathematical model for the water-carbon dioxide system.

The greatest lowering of pH of the water-carbon dioxide system happened at pressures up to about 5.516 MPa. At higher pressures the pH of the solution did not change significantly with further pressure increase. This trend of the pH of the binary system was observed both in the experimental pH values

Figure 4-1. Measured and predicted pH of water-carbon dioxide simulation system at pressures up to 34.48 MPa



as well as in the pH values predicted by the thermodynamic model. From a pressure of 0 to 5.516 MPa the variation in the measured pH was a drop of 2.53, whereas, from 5.516 MPa to 34.48 MPa the pH was lowered by only 0.14.

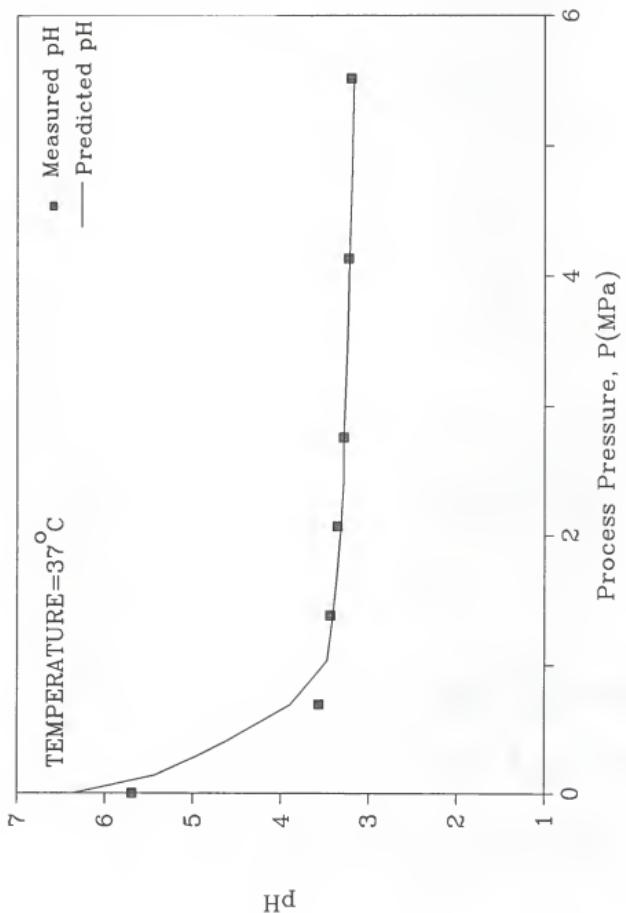
Using colorimetric methods, Moore and Buchanan (1930) found the same trend of pH lowering for aqueous solutions of carbon dioxide upto process pressures of 3.363 MPa, and at this process pressure, the measured pH of the aqueous solution was 3.3. Figure 4-2 compares the predicted pH values for the pure water-carbon dioxide system with the measured pH values in this study as well as the measured pH values measured colorimetrically by Moore and Buchanan (1930). There is a good agreement between the predicted and the measured pH values by both methods.

The sharp decrease followed by leveling in the pH values in the pure water-carbon dioxide system may be explained by the fact that since the pressure vessel is a closed system, the dissolution of carbon dioxide in water may be approaching a saturation limit at these pressures.

4.1.4.2 Effect of sugar on solubility of carbon dioxide

The measured pH values for pure water and an aqueous solution of 20% sucrose solution are given in Table 4-3. These values do not show any significant difference in the pH of the solution implying that up to the pressure of 5.86 MPa,

Figure 4-2. Measured and predicted pH of water-carbon dioxide simulation system at pressures upto 3.363 MPa



sucrose concentrations of up to 20% do not significantly affect the solubility of carbon dioxide in the solution.

4.1.4.3 Effect of process temperature on pH

Table 4-4 gives the measured pH values for the pure water-carbon dioxide system at three process temperatures of 32, 37 and 42°C over a pressure range of 0 to 5.861 MPa. Over this experimental temperature and pressure range, no significant change in the pH values was observed. However, the slightly lower pH values at the lower temperatures may be explained by the fact that the solubility of carbon dioxide in water is greater at low temperatures than at high temperatures (Weibe and Gaddy, 1940).

-1

4.2 Ascorbic Acid-Water-Carbon Dioxide Simulation System

4.2.1 Calculated Activity Coefficients

The calculated activity coefficients of the chemical species in the ascorbic acid-water-carbon dioxide simulation system include the activity coefficients already given in Table 4-1 for the pure water-carbon dioxide system and three other activity coefficients associated with the dissociation of ascorbic acid given in Table 4-5. Table 4-5 also gives the corresponding method used to calculate these activity coefficients. In order to calculate the variation of the activity coefficients with the process pressure, the compressibility coefficients and the partial molar volumes

Table 4-3. Measured pH values for pure water and sucrose solution

Process Pressure, P(MPa)	Average Measured pH of Pure Water \pm s	Average Measured pH of 20% Aqueous Solution of Sucrose \pm s
0	5.68 \pm 0.04	5.43 \pm 0.07
0.690	3.55 \pm 0.01	3.51 \pm 0.03
1.379	3.42 \pm 0.00	3.30 \pm 0.01
2.758	3.30 \pm 0.01	3.23 \pm 0.02
4.137	3.23 \pm 0.00	3.21 \pm 0.01
5.861	3.19 \pm 0.00	3.18 \pm 0.01

$H_0: \mu_{0\%} = \mu_{20\%}$

$H_a: \mu_{0\%} \neq \mu_{20\%}$

d=0.085

s_d=0.129

$t_{\text{calc.}} = 1.619 < t_{0.005} = 3.365$ (for df=5) \Rightarrow Rejection of Hypothesis

(pH values are not significantly different at 0.5% level.)

Table 4-4. Measured pH values of water-carbon dioxide system at different process temperatures

Process Pressure, P (MPa)	Measured pH at 32°C ± s	Measured pH at 37°C ± s	Measured pH at 42°C ± s
0	5.68 ± 0.04	5.70 ± 0.14	5.80 ± 0.00
0.690	3.55 ± 0.01	3.57 ± 0.01	3.66 ± 0.01
1.379	3.42 ± 0.00	3.44 ± 0.00	3.51 ± 0.01
2.069	3.35 ± 0.01	3.36 ± 0.01	3.42 ± 0.00
2.758	3.30 ± 0.01	3.29 ± 0.01	3.33 ± 0.01
4.137	3.23 ± 0.00	3.23 ± 0.01	3.26 ± 0.00
5.516	3.19 ± 0.00	3.20 ± 0.01	3.24 ± 0.01

$H_0: \mu_{32C} = \mu_{37C}$ and $\mu_{32C} = \mu_{42C}$

$H_a: \mu_{32C} \neq \mu_{37C}$ and $\mu_{32C} \neq \mu_{42C}$

$d_1 = 0.010$; $d_2 = 0.071$

$s_{d1} = 0.0157$; $s_{d2} = 0.0847$

$t_{\text{calc.}} = 1.681$ and $2.231 < t_{0.005} = 3.143$ (for $df=6$) \Rightarrow Rejection of Hypothesis (pH values are not significantly different at 0.5% level.)

have to be known for ascorbic acid and its dissociation ions. Since these values were not found in the thermodynamic literature and only very high process pressures can alter their values significantly, the activity coefficients for ascorbic acid and its two uni- and bi- valent ions were assumed to stay constant over the experimental pressure range.

Table 4-5. Calculated activity coefficients for the ascorbic acid-water-carbon dioxide system

Chemical Species	Calculated Activity Coefficient, γ	Estimation Method
$C_6H_8O_6$	0.190	UNIFAC
$C_6H_7O_6^-$	0.760	Debye-Huckel
$C_6H_6O_6^{--}$	0.360	Debye-Huckel

4.2.2 Comparison of Calculated and Experimental pH values

The pH data along with the pH values predicted by the thermodynamic model are given in Figures 4-3 and 4-4. As shown in the figures, the predicted pH values are in good agreement with the measured pH values. Tables A-2 and A-3 compare the measured and predicted values of pH for the ternary ascorbic acid-water-carbon dioxide system. The

Figure 4-3. Measured and predicted pH of the ascorbic acid-water-carbon dioxide system containing 1.107×10^{-3} M ascorbic acid (HI:A-LOW:C)

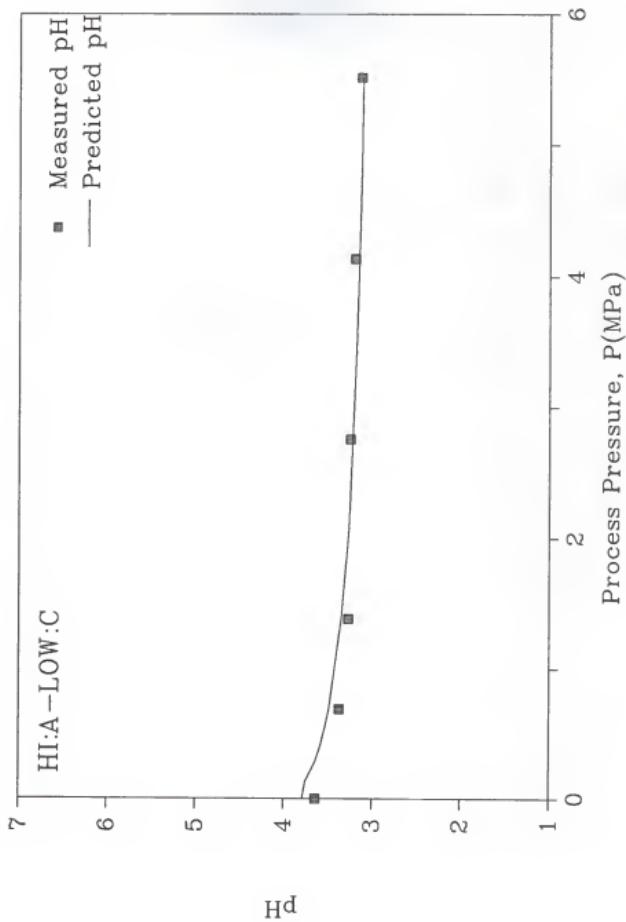
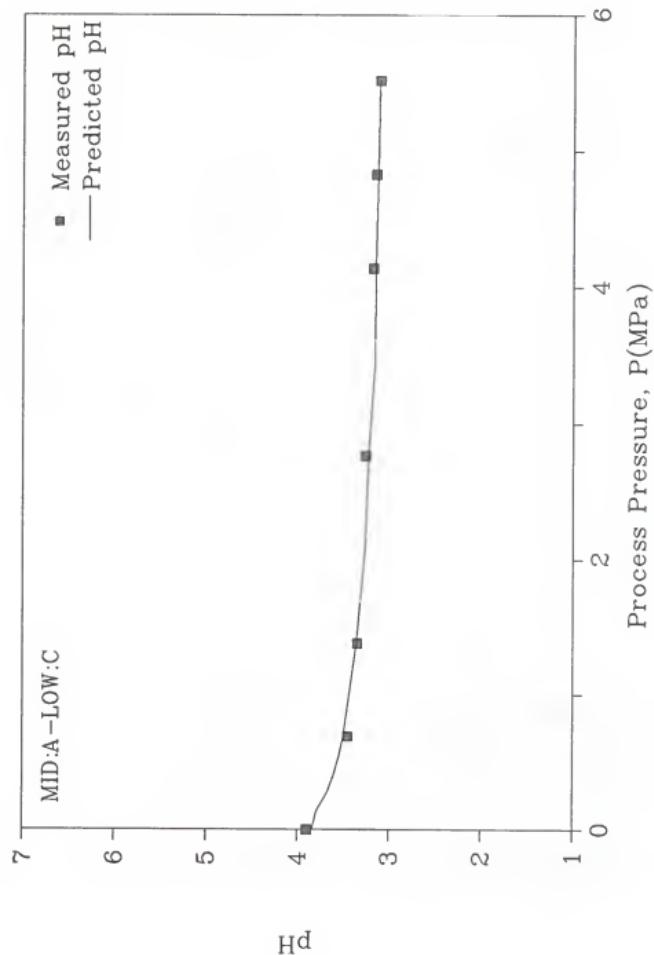


Figure 4-4. Measured and predicted pH of the ascorbic acid-water-carbon dioxide system containing 5.54×10^{-4} M ascorbic acid (MID:A-LOW:C)



concentrations of ascorbic acid in the aqueous solutions were 1.107×10^{-3} M and 5.540×10^{-4} M for the data given in Tables A-2 and A-3, respectively. Over the experimental pressure range, the pH of ascorbic acid-water-carbon dioxide solution starts at a lower value because of the presence of ascorbic acid in the solution, however, the pH drop from 0 to 5.516 MPa was not as great as the one observed in the binary water-carbon dioxide system. From the pH data it may be concluded that the presence of ascorbic acid had contributed to the reduced solubility of carbon dioxide in the solution.

4.3 Citric Acid-Water-Carbon Dioxide Simulation System

4.3.1 Calculated activity coefficients

The activity coefficients for the ternary system of citric acid-water-carbon dioxide simulation model includes the activity coefficients already given for the chemical species in the pure water-carbon dioxide system already given and the activity coefficients involved in the dissociation of citric acid. Table 4-6 gives the activity coefficients calculated for citric acid and its three dissociated ions along with the method of estimation.

Table 4-6. Calculated activity coefficients for the citric acid-water-carbon dioxide system

Chemical Species	Calculated Activity Coefficient, γ	Estimation Method
$C_6H_8O_7$	0.262	UNIFAC
$C_6H_7O_7^-$	0.760	Debye-Huckel
$C_6H_6O_7^{--}$	0.360	Debye-Huckel
$C_6H_5O_7^{---}$	0.115	Debye-Huckel

4.3.2 Comparison of calculated and experimental pH values

Tables A-4 and A-5 compare the pH values measured experimentally with the values predicted by the thermodynamic model for different concentrations of citric acids for the ternary simulation model. These pH values are plotted in Figures 4-5 and 4-6 where the average measured pH is indicated by data points and the pH predicted by the model is shown as solid lines. In general, the thermodynamic model closely predicted the actual pH of the simulation solution at different pressures for various concentrations of citric acid. As in the case with the ascorbic acid-water-carbon dioxide system, the pH drop over the experimental pressure range was not as large as the one for the pure water-carbon dioxide system. The same argument can be made that the presence of

Figure 4-5. Measured and predicted pH₄ of the citric acid-water-carbon dioxide system containing 6.08x10⁻⁴ M citric acid (LOW:A-HI:C)

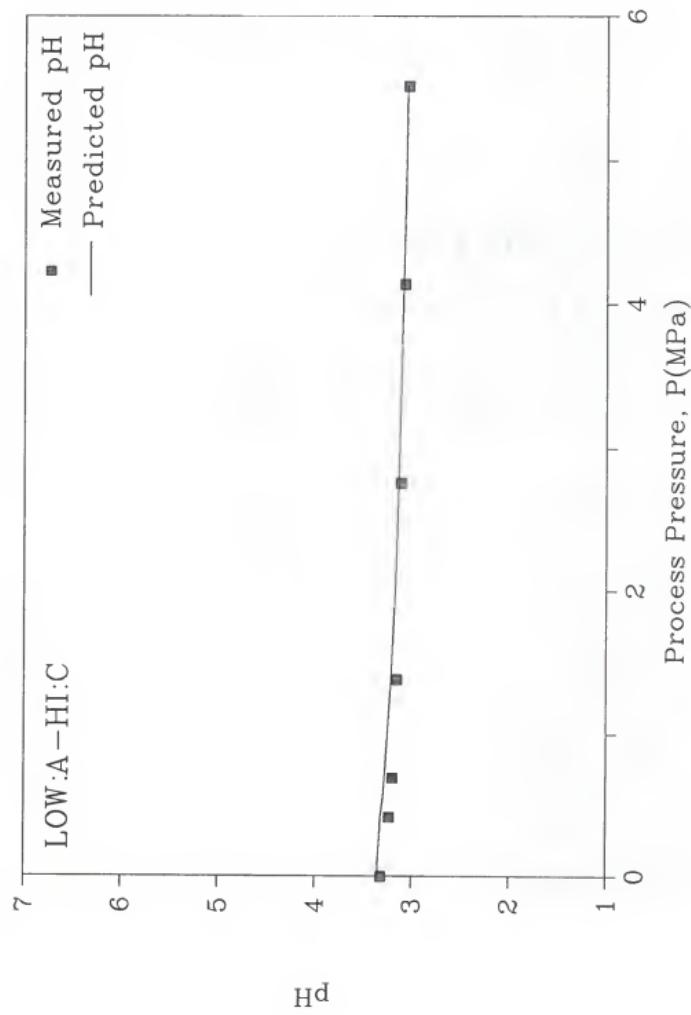
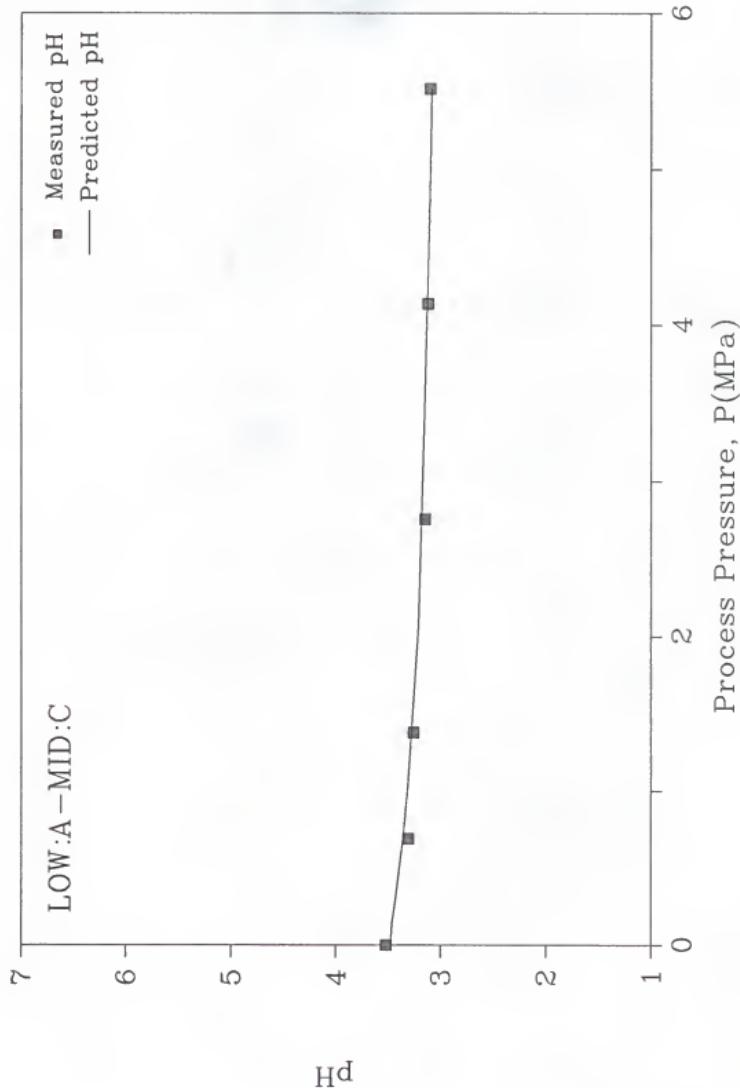


Figure 4-6. Measured and predicted pH of the citric acid-water-carbon dioxide system containing 3.04×10^{-4} M citric acid (LOW:A-MID:C)



ascorbic and/or citric acid may have decreased the solubility of carbon dioxide in the solution and consequently the smaller drop in the pH.

4.4 Ascorbic Acid-Citric Acid-Water-Carbon Dioxide Simulation System

4.4.1 Calculated Activity Coefficients

The activity coefficients used to develop the pH model for the quaternary simulation system of ascorbic acid-citric acid-water-carbon dioxide were the ones calculated for the three previous simulation models given in Tables 4-1, 4-5 and 4-6.

4.4.2 Comparison of Calculated and Experimental pH Values

Tables A-6 through A-10 give the measured and predicted pH values for the ascorbic acid-citric acid-water-carbon dioxide simulation system at different concentrations of ascorbic and citric acids. The plot of experimental and calculated pH values as functions of process pressure are given in Figures 4-7 to 4-10. As shown in these figures, the drop in pH over the experimental pressure range was even less than for the three previous simulation models. In the ascorbic acid-citric acid-water-carbon dioxide system, the presence of both ascorbic and citric acids seems to limit carbon dioxide solubility even more than in the other simulation systems.

Figure 4-7. Measured and predicted pH of the ascorbic acid-citric acid-water-carbon dioxide system containing 5.54×10^{-4} M ascorbic acid and 6.08×10^{-4} M citric acid (MID:A-HI:C)

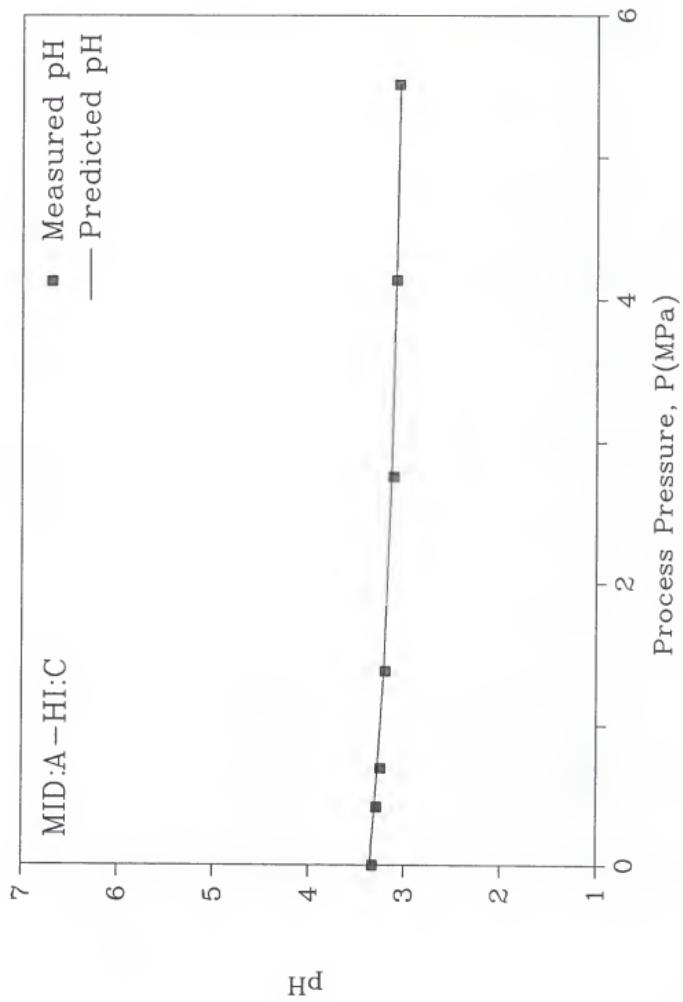


Figure 4-8. Measured and predicted pH of the ascorbic acid-citric acid-water-carbon dioxide system containing 1.107×10^{-3} M ascorbic acid and 6.08×10^{-4} M citric acid (H₂O:A-HC₂O:C)

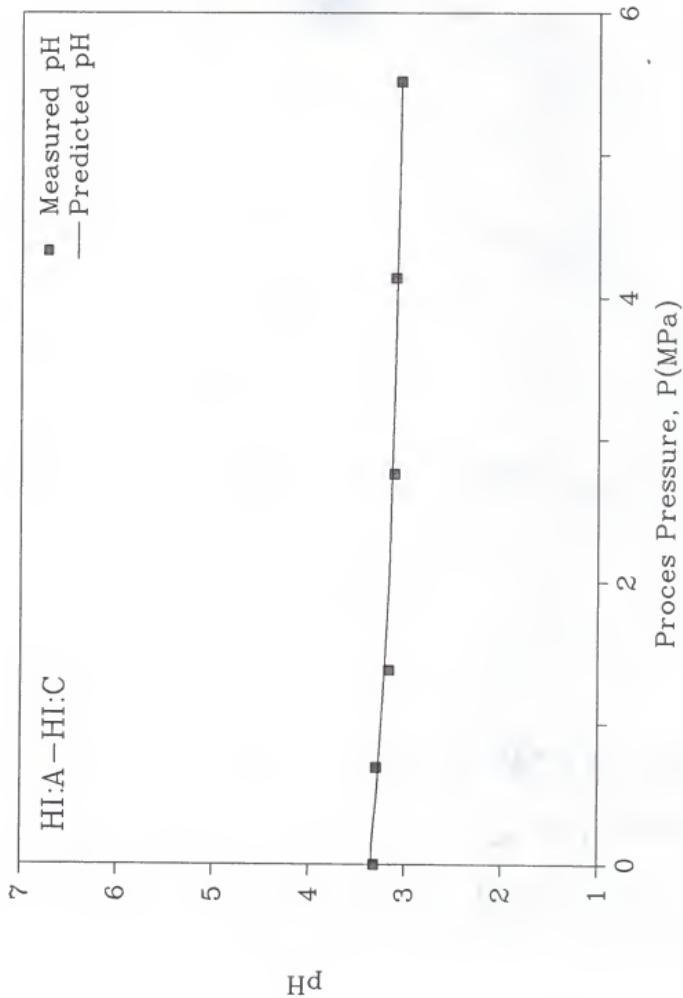


Figure 4-9. Measured and predicted pH of the ascorbic acid-citric acid-water-carbon dioxide system containing 1.107×10^{-3} M ascorbic acid and 3.04×10^{-4} M citric acid (HI:A-MID:C)

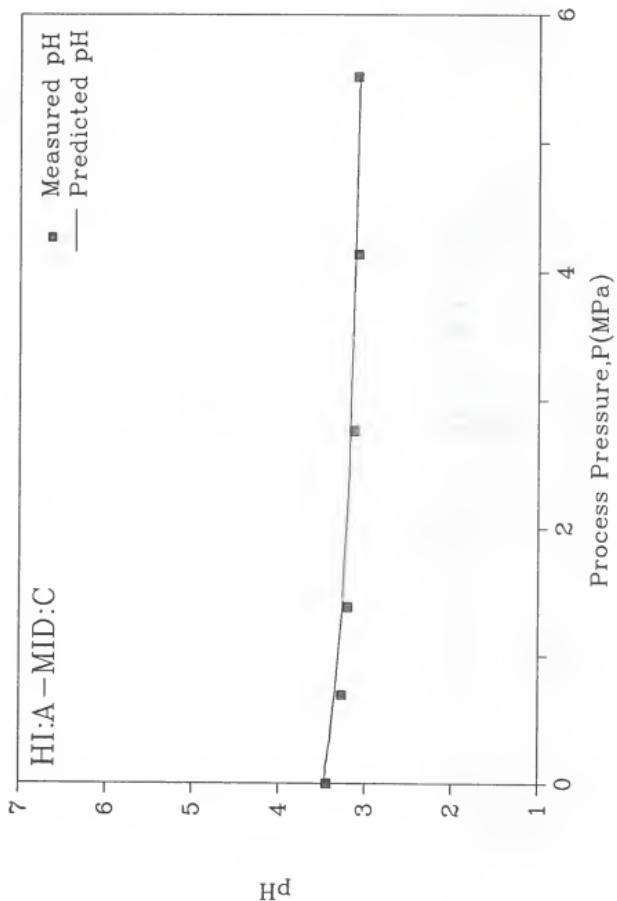
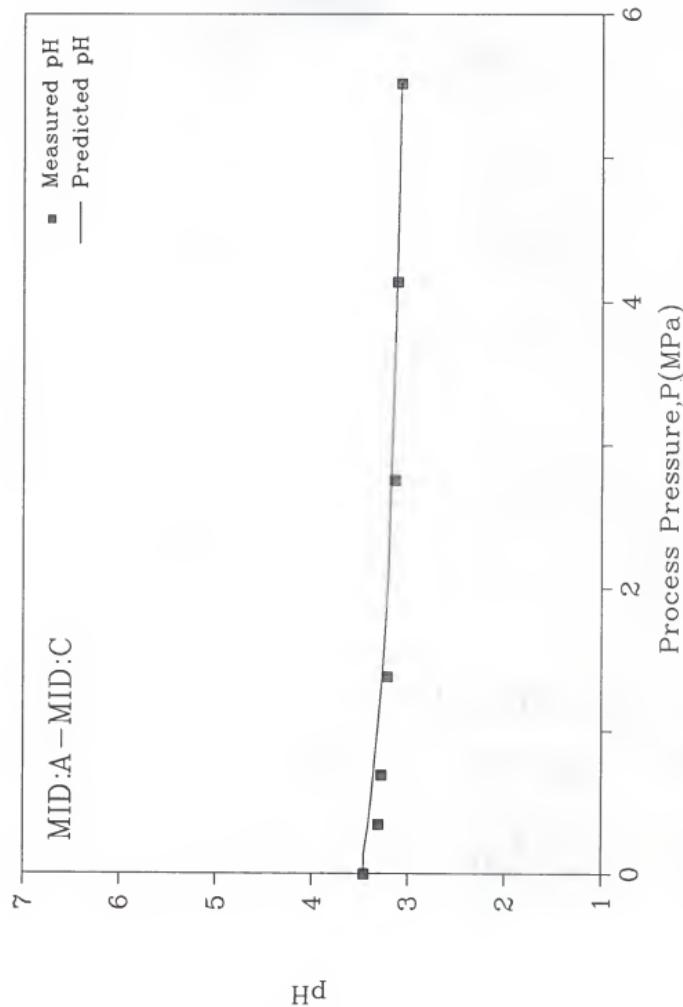


Figure 4-10. Measured and predicted pH of the ascorbic acid-citric acid-water-carbon dioxide system containing 5.54×10^{-4} M ascorbic acid and 3.04×10^{-4} M citric acid (MID:A-MID:C)



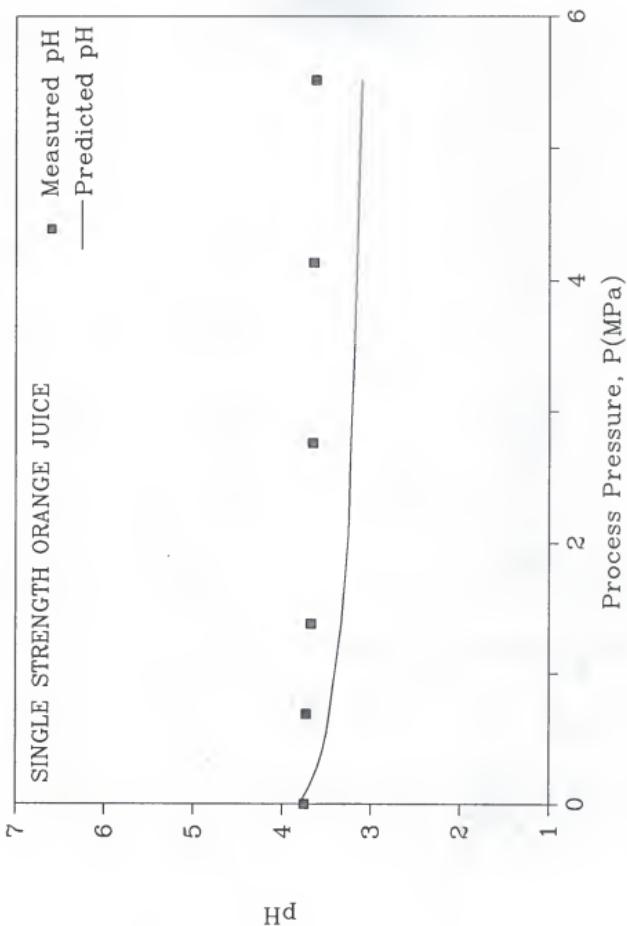
4.5 Single Strength Orange Juice

The measured pH values at different pressures of single strength orange juice are compared with the calculated pH of the ascorbic acid-citric acid-water-carbon dioxide model solution in Figure 4-11 and Table A-11. The pH of orange juice remained essentially constant over the experimental pressure range, while the ascorbic acid-citric acid-water-carbon dioxide model showed a modest initial decrease in pH with increasing pressure. This may be due to the fact that orange juice has a complex composition, and the presence of buffer systems in the juice can limit the solubility of carbon dioxide in the juice and maintain the concentration of the hydrogen ions at a fixed level. The presence of other organic acids in citrus juices has been indicated by several investigators. Nelson (1928) reported traces of malic acid in orange juice, and Hartman and Hillig (1934) found appreciable amounts of it in Florida Valencia oranges. Investigating the organic acids in grapefruit, Menchikowsky and Popper (1932) found that although the organic acids of the juice consist largely of citric acid (98.72%), they contain also malic (1.00%), oxalic (0.23%), and tartaric (0.05%) acids (percentage of the total amount of acid).

4.6 Model Sensitivity Analysis

Tables 4-7 and 4-8 show the sensitivity of the pH models to the 10% variation (decrease or increase) in the individual

Figure 4-11. Measured and predicted pH of single strength orange juice



activity coefficients and the reaction equilibrium constants. The activity coefficients of hydrogen ions, ascorbic acid and its univalent ion, citric acid and its uni- and bi-valent ions had a greater effect on the predicted pH value. Among the equilibrium constants, only the first dissociation constant of ascorbic acid (K_4) and the first dissociation constant of citric acid (K_6) were found to have some effect on the predicted pH value. Increasing the values for all the activity coefficients and equilibrium constants in the model at the same time resulted in a 3.5% increase in the predicted pH value. However, simultaneous increase of the activity coefficients and equilibrium constants may not indicate any important conclusions since there are both anions and cations present in the simulation systems.

The major variables which showed a significant effect on the value of predicted pH in the simulation models were the solubility of carbon dioxide in water in the water-carbon dioxide system, and the concentrations of ascorbic and citric acids in the three other simulation systems. In the water-carbon dioxide solution, doubling the solubility of carbon dioxide in the model resulted in a 3.2 and 4.7% decrease in the predicted pH value at 0 and 5.516 MPa process pressures, respectively. In the quaternary model, at atmospheric pressure, doubling the concentrations of ascorbic and citric acids resulted in a 0.7 and 3.9% drop in the predicted pH. The concentration of citric acid was found to have a much greater

effect on the predicted pH than the concentration of ascorbic acid for the two ternary as well as the quaternary models, which was supported by the experimental data.

4.7 Discussion of Results

The mathematical models developed for the four simulation systems accurately predicted the pH variation of these solutions as functions of process pressure and the concentrations of ascorbic and citric acids. From the expressions developed for the variation of the equilibrium constants and the activity coefficients as a function of process pressure, it was concluded that pressure has a significant effect only at very high values, and that it is the solubility of carbon dioxide in water which has a major effect on the pH of the solution. For the sugar concentration and process temperatures tested, it was shown that the pH was not a strong function of sugar concentration or process temperature.

The predicted and measured pH values for the binary water-carbon dioxide system showed the greatest drop in solution pH from 5.70 to 3.20 over the pressure range of 0 to 5.52 KPa at a temperature of 37°C. This implicated that substantially greater quantities of carbon dioxide were dissolved to produce carbonic acid in the binary water-carbon dioxide system than in the other simulation systems resulting in the lowering of pH values in the system during the

pressurization process. The pH drop from the initial value at atmospheric pressure in the three simulation systems of ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide, and ascorbic acid-citric acid-water-carbon dioxide was found to be considerably less than in the binary system mainly because of the presence of ascorbic acid and citric acid in the solution initially, which presumably limited the solubility of carbon dioxide and the subsequent production of carbonic acid.

This behavior of the system pH was even more pronounced in the experiments performed with single strength orange juice over the pressure range of 0 to 5.57 MPa. The pH of the orange juice dropped by only 3.2% whereas for the pure water-carbon dioxide solution the pH drop was 43.86% over the same pressure range. From Figure 4-11 which shows both the measured pH of the orange juice and the pH values predicted by the ascorbic acid-citric acid-water-carbon dioxide model, it may be concluded that the complex composition of orange juice, or citrus juice in general, and the existing buffer systems are a major factor in the low sensitivity of pH with process pressure. The small pH drop also indicates that cloud stability and pectinesterase inactivation during the high pressure carbon dioxide process may not be entirely due to low pH inactivation of the enzyme, and that other mechanisms of inactivation may be responsible for cloud stability.

Table 4-7. Sensitivity analysis of the pH model at atmospheric pressure and 37°C with the variation in activity coefficients

Activity coefficient	-10% Variation	0% Variation	+10% Variation
H ⁺	3.365	3.343	3.324
OH ⁻	3.343	3.343	3.343
CO ₂	3.343	3.343	3.343
H ₂ CO ₃	3.344	3.343	3.343
HCO ₃ ⁻	3.344	3.343	3.343
CO ₃ ²⁻	3.343	3.343	3.343
C ₆ H ₈ O ₆	3.344	3.343	3.343
C ₆ H ₇ O ₆ ⁻	3.341	3.343	3.345
C ₆ H ₆ O ₆ ²⁻	3.343	3.343	3.343
C ₆ H ₈ O ₇	3.362	3.343	3.326
C ₆ H ₇ O ₇ ⁻	3.327	3.343	3.358
C ₆ H ₆ O ₇ ²⁻	3.341	3.343	3.346
C ₆ H ₅ O ₇ ³⁻	3.343	3.343	3.343

Table 4-8. Sensitivity analysis of the pH model at atmospheric pressure and 37°C with the variation in the equilibrium constants

Equilibrium constant	-10% Variation	0% Variation	+10% Variation
K_w	3.343	3.343	3.343
K_1	3.343	3.343	3.343
K_2	3.344	3.343	3.343
K_3	3.343	3.343	3.343
K_4	3.346	3.343	3.341
K_5	3.343	3.343	3.343
K_6	3.362	3.343	3.326
K_7	3.343	3.343	3.343
K_8	3.343	3.343	3.343

CHAPTER 5
CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDY

5.1 Conclusions

Thermodynamic correlations were successfully applied to a set of four citrus simulation systems to predict their pH variation when processed with supercritical carbon dioxide, with the following conclusions drawn from this study:

1. Mathematical expressions can be developed to model the behavior of food systems such as fruit juices through a thermodynamic approach. All of the pH models developed for the four simulation solutions of pure water-carbon dioxide, ascorbic acid-water-carbon dioxide, citric acid-water-carbon dioxide and ascorbic acid-citric acid-water-carbon dioxide, accurately predicted the pH values which were measured experimentally. Over the experimental pressure range, the lowering of the pH of the simulation systems was mostly due to the solubility of carbon dioxide and/or the concentrations of acids in the solution rather than the variation of the equilibrium constants or the activity coefficients with pressure.

2. The pH values for both the quaternary simulation system and single strength orange juice were found to be weak functions of process pressure but very strong functions of system composition. The pH of the orange juice was less sensitive to process pressure than the pH of the ascorbic

acid-citric acid-water-carbon dioxide system. This may be due to the complex composition of citrus juices which, with their natural buffer systems, can limit the solubility of carbon dioxide and consequently limit the production of carbonic acid in the solution. This implication was deduced from the observation that the pH drop in the binary system of water-carbon dioxide with a relatively simple composition was 43.86%, whereas the pH drop for the single strength orange juice was only 3.2% over the same pressure range. Generally as the composition of the simulation systems became more complex, less carbon dioxide was dissolved in the solutions. Since this limits the generation of carbonic acid, the observed pH drop was smaller.

3. The pH values predicted by the models for the four simulation systems can provide information about pH variations of not only citrus juices but also citrus beverages during the carbonation process. From the pH studies with the four simulation systems it was concluded that the pH drop for a citrus beverage during the carbonation process can be composition dependent and/or pressure dependent.

4. The small pH drop in orange juice and the ternary and quaternary models did not support the hypothesis that pectinesterase was inactivated by low pH in the high pressure carbon dioxide process. Arreola (1990) reported 100% inactivation of pectinesterase in orange juice treated

with supercritical carbon dioxide at pressures between 7.4 and 34 MPa and temperatures of 35 to 60°C. However, the pH behavior of orange juice was not measured during those experiments and was unknown. The mechanism of pectinesterase inactivation and the subsequent cloud stability in the high pressure carbon dioxide treatment of citrus juices may only be partly due to lowering of the pH if at all; it may be strictly a pressure-related phenomena.

5.2 Suggestions For Future Study

Future works in the area of citrus cloud stability in the supercritical carbon dioxide process can focus on the mechanism of pectinesterase inactivation and its relation to the pH. More studies on the inactivation of pectinesterase are required to not only find out what the mechanism is, but also to be able to quantify the percentage of inactivation of pectinesterase. The same way thermodynamics and reaction equilibria were applied in this study to find mathematical expressions for the pH variation of the simulation systems, principles of reaction equilibria and enzyme kinetics can be used together to quantitatively model cloud stability in citrus juices as a function of the supercritical process conditions.

APPENDIX A
TABLES OF PREDICTED AND MEASURED PH VALUES

Table A-1. Predicted and measured pH values at different process pressures for the pure water-carbon dioxide simulation system

Process Pressure, P(MPa)	Average Experimental pH ± s	Predicted pH
0	5.75 ± 0.05	5.59
0.3448	4.59 ± 0.09	4.79
0.6895	3.48 ± 0.06	3.90
1.379	3.48 ± 0.06	3.41
2.758	3.48 ± 0.06	3.08
4.138	3.27 ± 0.02	3.21
5.516	3.22 ± 0.03	3.17
4.138	3.48 ± 0.06	3.17
10.343	3.15 ± 0.04	3.12
13.790	3.15 ± 0.03	3.11
17.238	3.14 ± 0.04	3.11
20.685	3.14 ± 0.04	3.09
24.133	3.14 ± 0.04	3.09
20.685	3.12 ± 0.03	3.08
31.028	3.10 ± 0.04	3.07
34.475	3.08 ± 0.04	3.06

Table A-2. Comparison of measured and predicted pH values of the ascorbic acid-water-carbon dioxide system containing 1.107×10^{-3} M ascorbic acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.74 \pm 0.15	3.85
0.690	3.47 \pm 0.08	3.51
1.379	3.27 \pm 0.04	3.39
2.758	3.25 \pm 0.05	3.28
4.137	3.20 \pm 0.01	3.21
5.516	3.13 \pm 0.03	3.16

Table A-3. Comparison of measured and predicted pH values of the ascorbic acid-water-carbon dioxide system containing 5.540×10^{-4} M ascorbic acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.90 \pm 0.08	3.98
0.690	3.90 \pm 0.08	3.53
1.379	3.35 \pm 0.11	3.40
2.758	3.26 \pm 0.03	3.26
4.137	3.19 \pm 0.01	3.19
5.516	3.15 \pm 0.03	3.15

Table A-4. Comparison of measured and predicted pH for the citric acid-water-carbon dioxide system with 6.08×10^{-4} M citric acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.32 \pm 0.04	3.35
0.414	3.23 \pm 0.00	3.32
0.690	3.20 \pm 0.05	3.28
1.379	3.16 \pm 0.07	3.22
2.758	3.12 \pm 0.02	3.14
4.137	3.08 \pm 0.06	3.10
5.516	3.05 \pm 0.03	3.06

Table A-5. Comparison of measured and predicted pH for the citric acid-water-carbon dioxide system with 3.04×10^{-4} M citric acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.52 \pm 0.04	3.36
0.690	3.31 \pm 0.07	3.36
1.379	3.26 \pm 0.01	3.28
2.758	3.15 \pm 0.03	3.18
4.137	3.12 \pm 0.04	3.12
5.516	3.10 \pm 0.00	3.09

Table A-6. Comparison of measured and predicted pH for the ascorbic acid-citric acid-water-carbon dioxide system with 5.54×10^{-4} M ascorbic acid and 6.08×10^{-4} M citric acid.

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.33 \pm 0.09	3.35
0.276	3.29 \pm 0.05	3.32
0.690	3.20 \pm 0.04	3.23
1.379	3.20 \pm 0.04	3.22
2.758	3.12 \pm 0.06	3.10
4.137	3.29 \pm 0.05	3.10
5.516	3.07 \pm 0.02	3.06

Table A-7. Comparison of measured and predicted pH for the ascorbic acid-citric acid-water-carbon dioxide system with 1.107×10^{-3} M ascorbic acid and 6.08×10^{-4} M citric acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.32 \pm 0.06	3.34
0.690	3.30 \pm 0.02	3.27
1.379	3.17 \pm 0.05	3.21
2.758	3.12 \pm 0.08	3.13
4.137	3.11 \pm 0.01	3.09
5.516	3.06 \pm 0.03	3.06

Table A-8. Comparison of measured and predicted pH for ascorbic acid-citric acid-water-carbon dioxide system with 1.107×10^{-3} M ascorbic acid and 3.04×10^{-4} M citric acid

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.44 \pm 0.03	3.35
0.690	3.27 \pm 0.05	3.35
1.379	3.20 \pm 0.11	3.26
2.758	3.13 \pm 0.08	3.17
4.137	3.09 \pm 0.04	3.12
5.516	3.10 \pm 0.07	3.08

Table A-9. Comparison of measured and predicted pH values for the ascorbic acid-citric acid-water-carbon dioxide system with 5.54×10^{-4} M ascorbic acid and 3.04×10^{-4} M citric acid.

Process Pressure, P(MPa)	Measured pH \pm s	Predicted pH
0	3.46 \pm 0.13	3.47
0.345	3.31 \pm 0.05	3.47
0.690	3.28 \pm 0.02	3.18
1.379	3.22 \pm 0.04	3.27
2.758	3.14 \pm 0.02	3.18
4.137	3.12 \pm 0.05	3.13
5.516	3.08 \pm 0.01	3.09

Table A-10. Comparison of measured and predicted pH of single strength orange juice

Process Pressure, P(MPa)	Measured pH ± s	Predicted pH
0	3.75 ± 0.13	3.80
0.690	3.73 ± 0.05	3.80
1.379	3.68 ± 0.06	3.34
2.758	3.66 ± 0.02	3.23
4.137	3.65 ± 0.03	3.16
5.516	3.63 ± 0.00	3.11

APPENDIX B

FORTRAN PROGRAM TO SOLVE FOR
EQUILIBRIUM ACTIVITIES USING
NEWTON-RAPHSON ITERATION METHOD

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*****
* MODEL FOR THE PREDICTION OF PH AS A FUNCTION OF PRESSURE AND
* TEMPERATURE FOR THE SIMULATION SYSTEMS OF A) PURE WATER-CARBON
* DIOXIDE ; B) ASCORBIC ACID-CITRIC ACID-WATER-CARBON DIOXIDE
*****
* THIS PROGRAM CALCULATES PH OF THE SIMULATION SYSTEM FOR A SPE-
* CIFIED PROCESS TEMPERATURE AND PRESSURE , AND CONCENTRATIONS
* OF ASCORBIC ACID AND CITRIC ACID USING THE NEWTON-RAPHSON
* ITERATION METHOD BY SOLVING A SET OF SIMULTANEOUS EQUATIONS FOR
* THE EQUILIBRIUM CONCENTRATIONS OF THE CHEMICAL SPECIES PRESENT
* IN THE SYSTEM. THE PH OF THE SOLUTION IS CALCULATED BY TAKING
* THE NEGATIVE LOG OF THE CONCENTRATION OF HYDROGEN IONS TO
* WHICH THE ITERATION VARIABLES CONVERGE.
*****
* DACTI=ACTIVITY COEFFICIENT OF SPECIES I
* DX(I)=EQUILIBRIUM CONCENTRATION OF SPECIES I (MOLES/LITER)
* SPECIES 1= H+ IONS
* SPECIES 2= OH- IONS
* SPECIES 3= CO2 (CARBON DIOXIDE)
* SPECIES 4= H2CO3 (CARBONIC ACID)
* SPECIES 5= HCO3- IONS
* SPECIES 6= CO3-- IONS
* SPECIES 7= C6H7O6- IONS
* SPECIES 8= C6H6O6-- IONS
* SPECIES 9= C6H7O7- IONS
* SPECIES 10= C6H6O7-- IONS
* SPECIES 11= C6H5O7--- IONS
*****
* DKW=DISSOCIATION CONSTANT FOR DISSOCIATION OF WATER
* DKJ=DISSOCIATION CONSTANT FOR THE REACTION J
* REACTION 2= DISSOCIATION OF CARBONATE ION
* REACTION 3= DISSOCIATION OF CARBONIC ACID TO CARBONATE ION
* REACTION 4= DISSOCIATION OF CARBONIC ACID TO CARBON DIOXIDE
* AND WATER
* REACTION 5= DISSOCIATION OF ASCORBIC ACID TO C6H7O6- ION
* REACTION 6= DISSOCIATION OF C6H7O6- TO C6H6O6--
* REACTION 7= DISSOCIATION OF CITRIC ACID TO C6H7O7-
* REACTION 8= DISSOCIATION OF C6H7O7- TO C6H6O7--
* REACTION 9= DISSOCIATION OF C6H6O7-- TO C6H5O7---
*****
* DSOL=SOLUBILITY OF CARBON DIOXIDE IN WATER
* DFUN2=INTERPOLATION FUNCTION FOR CALCULATING THE SOLUBILITY
*****
INTEGER SYS,I,J,L,K,Q
DOUBLE PRECISION DACT1,DACT2,DACT3,DACT4,DACT5,DACT6
DOUBLE PRECISION DKW,DK2,DK3,DK4,DK5,DH,DFH,DDFH,DNEWH
DOUBLE PRECISION DXH2O,DA,DB,DC,DD,DE,DF,DP,DPH,DS,DETM
DOUBLE PRECISION DX(11),B(11),C(11,11),B1(11),DXX(11),DK6
DOUBLE PRECISION DTNRM,DXCIT,DXASC,DACT7,DACT8,DACT9
DOUBLE PRECISION DACT10,DACT11,DK7,DK8,DK9,DK10,DK11
DOUBLE PRECISION PD,CC
DOUBLE PRECISION P(90),T(90),S(90)
```

```

DOUBLE PRECISION DEN,DSOL,DTEMP,DFUN2
PRINT*, 'ENTER SIMULATION MODEL SYSTEM: '
PRINT*, '1 FOR PURE WATER-CARBON DIOXIDE SYSTEM'
PRINT*, 'OR 2 FOR ASCORBIC-CITRIC-WATER-CARBON DIOXIDE
SYSTEM'
READ*,SYS
*****
* INTERPOLATION ROUTINE FOR THE CALCULATION OF CARBON DIOXIDE
* SOLUBILITY AT THE SPECIFIC TEMPERATURE AND PRESSURE
*****
DATA (P(N),N=1,9) /9*25.0D+00/
DATA (P(N),N=10,18) /9*50.0D+00/
DATA (P(N),N=19,27) /9*75.0D+00/
DATA (P(N),N=28,36) /9*100.0D+00/
DATA (P(N),N=37,45) /9*150.0D+00/
DATA (P(N),N=46,54) /9*200.0D+00/
DATA (P(N),N=55,63) /9*300.0D+00/
DATA (P(N),N=64,72) /9*400.0D+00/
DATA (P(N),N=73,81) /9*500.0D+00/
DATA (P(N),N=82,90) /9*700.0D+00/
*****
DATA (T(N),N=1,9) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=10,18) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=19,27) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=28,36) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=37,45) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=46,54) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=55,63) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=64,72) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=73,81) /12,18,25,31.04,35,40,50,75,100/
DATA (T(N),N=82,90) /12,18,25,31.04,35,40,50,75,100/
*****
DATA(S(N),N=1,9)/6.88,3.86,4.59,2.80,2.56,2.30,1.92,1.35,1.06/
DATA(S(N),N=10,18)/7.03,6.33,5.38,4.77,4.39,4.02,3.41,2.49,2.01/
DATA(S(N),N=19,27)/7.18,6.69,6.17,5.8,5.51,5.1,4.45,3.37,2.82/
DATA(S(N),N=28,36)/7.27,6.72,6.28,5.97,5.76,5.5,5.07,4.07,3.49/
DATA(S(N),N=37,45)/7.59,7.07,6.60,6.25,6.03,5.81,5.47,4.86,4.49/
DATA(S(N),N=46,54)/7.6,7.21,6.91,6.48,6.29,6.28,5.76,5.27,5.08/
DATA(S(N),N=55,63)/7.86,7.35,7.23,6.88,6.68,6.59,6.2,5.83,5.84/
DATA(S(N),N=64,72)/8.12,7.77,7.54,7.27,7.06,6.89,6.58,6.3,6.4/
DATA(S(N),N=73,81)/8.38,8.19,7.85,7.65,7.51,7.26,6.96,6.4,6.96/

```

```

DATA(S(N),N=82,90)/8.9,8.61,8.47,8.42,8.34,7.93,7.58,7.43,7.61/
*****
*****  

IF (SYS.EQ.1) THEN
PRINT*, '-----'  

101 PRINT*, 'ENTER PRESSURE (PSI)='
READ*, DP
IF (DP.LT.0.0D+00) THEN
STOP
ELSE
GOTO 110
ENDIF  

110 PRINT*, 'ENTER TEMPERATURE (C)='
READ*, DTEMP
PRINT*, '-----'
DP=DP/14.7D+00
DO 10 Q=1,1
N=90
M=9
DX(1)=1.0D-4
DO 780 I=2,6
DX(I)=1.0D-4
780 CONTINUE
IF (DP.LE.24.0D+00) THEN
DSOL=((0.5942D+00)*(DP-1.0)+0.696D+00)/2.4D+01
ELSE
DSOL=DFUN2(DP,DTEMP,N,M,P,T,S)*2.273D-01
ENDIF  

*****  

DKW=(10.0D+00)**((-13.677D+00)+(0.00036D+00)*DP)
DK2=(10.0D+00)**((0.0005D+00)*DP-10.2515D+00)
DK3=(10.0D+00)**((0.0005D+00)*DP-6.3662D+00)
DK4=(10.0D+00)**((-6.355D+00)+(0.00048D+00)*DP)
*****  

IF (DP.LE.7.0D+00) THEN
DACT1=(0.0005D+00*DEXP(DP-1.0D+00))
ELSE
DACT1=0.830D+00
ENDIF  

DACT2=(10.0D+00)**((-0.11926D+00)-(2.575D-06)*DP*DP+(1.03D-04)*DP
)
DACT3=1.0D+00
DACT4=(10.0D+00)**((+0.0005D+00)-(0.000479D+00)*DP)  

DACT5=(10.0D+00)**((-0.11068D+00)+(1.421D-05)*DP-(3.55D-07)*DP*DP
)
DACT6=(10.0D+00)**((-0.44362D+00)-(6.661D-06)*DP*DP+(1.332D-05)
+ *DP)
*****
```

```

DO 20 J=1,100
DO 500 I=1,6
DO 600 K=1,6
C(I,K)=0.0D+00
600 CONTINUE
500 CONTINUE
C(2,1)=1.0D+00
C(3,1)=-DACT1*DACT2*DX(2)
C(4,1)=-DACT1*DACT6*DX(6)
C(5,1)=-DACT1*DACT5*DX(5)
C(1,3)=1.0D+00
C(1,4)=1.0D+00
C(1,5)=1.0D+00
C(1,6)=1.0D+00
C(2,2)=-1.0D+00
C(2,5)=-1.0D+00
C(2,6)=-2.0D+00
C(3,2)=-DACT1*DACT2*DX(1)
C(4,5)=DACT5*DK2
C(4,6)=-DACT1*DACT6*DX(1)
C(5,4)=DACT4*DK3
C(5,5)=-DACT1*DACT5*DX(1)
C(6,3)=-DACT3
C(6,4)=DACT4*DK4
*****
B(1)=DX(3)+DX(4)+DX(5)+DX(6)-DSOL
B(2)=DX(1)-DX(2)-DX(5)-2.0D+00*DX(6)
B(3)=-DACT1*DACT2*DX(1)*DX(2) + DKW
B(4)=-DACT1*DACT6*DX(1)*DX(6) + DACT5*DK2*DX(5)
B(5)=-DACT1*DACT5*DX(1)*DX(5) + DACT4*DK3*DX(4)
B(6)=-DACT3*DX(3) + DACT4*DK4*DX(4)
*****
N=6
*****
CALL INVDET(C,N,DTNRM,DETM)
DO 700 K=1,6
    B1(K)=0.0D+00
    DO 710 L=1,6
        B1(K)=C(K,L)*B(L)+B1(K)
710    CONTINUE
700    CONTINUE
*****
DO 720 L=1,6
    DXX(L)=DX(L)-B1(L)
720    CONTINUE
    IF(DXX(2).GT.0.0D+00.AND.DXX(3).GT.0.0D+00.AND.DXX(4).GT.
+    0.0D+00.AND.DXX(5).GT.0.0D+00.AND.DXX(6).GT.0.0D+00.AND.
+    DXX(1).GT.0.0D+00.AND.DABS(DXX(1)-DX(1)).LE.1.0D-9) THEN
    IF(DXX(1).GT.0.0D+00) THEN
    PH=-DLOG10(DXX(1)*DACT1)
    PRINT*, '----PH=' ,PH
    PRINT*, '-----'

```

```

ENDIF
GOTO 101
ENDIF
DO 22 I=1,6
DX(I)=DXX(I)
22  CONTINUE
20  CONTINUE
*****
10  CONTINUE
*****
ELSEIF (SYS.EQ.2) THEN
*****
*****DO 11 Q=1,100
PRINT*, '-----'
PRINT*, 'ENTER PRESSURE (PSI)='
READ*, DP
PRINT*, '-----'
IF(DP.EQ.-1.0D+00) GOTO 5000
DXCIT=3.04D-04
DXASC=1.107D-03
DTEMP=37.0D+00
DP=DP/14.7D+00
N=90
M=9
DX(1)=1.0D-04
DX(2)=1.0D-04
DX(3)=0.1D-04
DX(4)=0.1D-04
DX(5)=0.1D-04
DX(6)=0.1D-04
DX(7)=4.0D-04
DX(8)=4.0D-04
DX(9)=4.0D-04
DX(10)=4.0D-04
DX(11)=4.0D-04
IF (DP.LE.24.0D+00) THEN
  DSOL=((0.5942D+00)*(DP-1.0)+0.696D+00)/2.4D+01
ELSE
  DSOL=DFUN2(DP,DTEMP,N,M,P,T,S)*2.273D-01
ENDIF
*****
DKW=(10.0D+00)**((-13.677D+00)+(0.00036D+00)*DP)
DK2=(10.0D+00)**((0.0005D+00)*DP-10.2515D+00)
DK3=(10.0D+00)**((0.0005D+00)*DP-6.3662D+00)
DK4=(10.0D+00)**((-6.355D+00)+(0.00048D+00)*DP)
DK5=7.94D-05
DK6=1.62D-12
DK10=1.73D-05
DK11=4.02D-07
*****
*
```

```

DACT1=0.830D+00

DACT2=(10.0D+00)**((-0.11926D+00)-(2.575D-06)*DP*DP+(1.03D-04)*DP
)
DACT3=1.0D+00
DACT4=(10.0D+00)**((+0.0005D+00)-(0.000479D+00)*DP)

DACT5=(10.0D+00)**((-0.11068D+00)+(1.421D-05)*DP-(3.55D-07)*DP*DP
)
DACT6=(10.0D+00)**((-0.44362D+00)-(6.661D-06)*DP*DP+(1.332D-05)
+ *DP)
DACT7=0.76D+00
DACT8=0.36D+00
DACT9=0.76D+00
DACT10=0.36D+00
DACT11=0.115D+00
*****
DO 21 J=1,200
DO 501 I=1,11
DO 601 K=1,11
C(I,K)=0.0D+00
601 CONTINUE
501 CONTINUE
C(2,1)=1.0D+00
C(3,1)=-DACT1*DACT2*DX(2)
C(4,1)=-DACT1*DACT6*DX(6)
C(5,1)=-DACT1*DACT5*DX(5)
C(1,3)=1.0D+00
C(1,4)=1.0D+00
C(1,5)=1.0D+00
C(1,6)=1.0D+00
C(2,2)=-1.0D+00
C(2,5)=-1.0D+00
C(2,6)=-2.0D+00
C(3,2)=-DACT1*DACT2*DX(1)
C(4,5)=DACT5*DK2
C(4,6)=-DACT1*DACT6*DX(1)
C(5,4)=DACT4*DK3
C(5,5)=-DACT1*DACT5*DX(1)
C(6,3)=-DACT3
C(6,4)=DACT4*DK4
C(7,1)=DX(7)*DACT1*DACT7
C(7,7)=DX(1)*DACT1*DACT7
C(8,1)=DX(8)*DACT1*DACT8
C(8,7)=-DK6*DACT7
C(8,8)=DX(1)*DACT1*DACT8
C(2,7)=-1.0D+00
C(2,8)=-2.0D+00
C(2,9)=-1.0D+00
C(2,10)=-2.0D+00
C(2,11)=-3.0D+00

```

```

C(9,1)=-DACT9*DACT1*DX(9)
C(9,9)=-DACT1*DX(1)*DACT9
C(10,1)=-DACT10*DACT1*DX(10)
C(10,9)=DACT9*DK10
C(10,10)=-DACT10*DACT1*DX(1)
C(11,1)=-DACT11*DACT1*DX(11)
C(11,10)=DACT10*DK11
C(11,11)=-DACT11*DACT1*DX(1)
*****
B(1)=DX(3)+DX(4)+DX(5)+DX(6)-DSOL

B(2)=DX(1)-DX(2)-DX(5)-(2.0D+00)*DX(6)-DX(7)-(2.0D+00)*DX(8)
+ -DX(9)-2.0D+00*DX(10)-3.0D+00*DX(11)
B(3)=-DACT1*DACT2*DX(1)*DX(2) + DKW
B(4)=-DACT1*DACT6*DX(1)*DX(6) + DACT5*DK2*DX(5)
B(5)=-DACT1*DACT5*DX(1)*DX(5) + DACT4*DK3*DX(4)
B(6)=-DACT3*DX(3) + DACT4*DK4*DX(4)
B(7)=DACT1*DX(1)*DX(7)*DACT7-(7.94D-05)*DXASC*0.19D+00
B(8)=DACT1*DX(1)*DX(8)*DACT8-1.62D-12*DX(7)*DACT7
B(9)=(0.262D+00*7.45D-04)*DXCIT-(DACT9*DACT1*DX(1)*DX(9))
B(10)=DACT9*1.73D-05*DX(9)-DACT10*DACT1*DX(1)*DX(10)
B(11)=DACT10*4.02D-07*DX(10)-DACT11*DACT1*DX(1)*DX(11)
*****
N=11
*****
CALL INVDET(C,N,DTNRM,DETM)
DO 701 K=1,11
    B1(K)=0.0D+00
    DO 711 L=1,11
        B1(K)=C(K,L)*B(L)+B1(K)
711    CONTINUE
701    CONTINUE
*****
DO 721 L=1,11
    DXX(L)=DX(L)-B1(L)
721    CONTINUE
IF(DXX(2).GT.0.0D+00.AND.DXX(3).GT.0.0D+00.AND.DXX(4).GT.
+ 0.0D+00.AND.DXX(5).GT.0.0D+00.AND.DXX(6).GT.0.0D+00.AND.
+ DXX(1).GT.0.0D+00.AND.DABS(DXX(1)-DX(1)).LE.1.0D-9) THEN
IF(DXX(1).GT.0.0D+00) THEN
PH=-DLOG10(DXX(1)*DACT1)
PRINT*, '----PH=' , PH
PRINT*, 'PRESS(PSI)' , DP*14.7D+00
PRINT*, '-----' ,
ENDIF
GOTO 11
ENDIF
DO 23 I=1,11
    DX(I)=DXX(I)
23    CONTINUE
21    CONTINUE
*****

```

```

11  CONTINUE
ENDIF
5000 END
*****
* FUNCTION SUBPROGRAM
*****
DOUBLE PRECISION FUNCTION DFUN2(A,B,N,M,P,T,S)
DOUBLE PRECISION A,B,YT1,YT2
DOUBLE PRECISION P(90),T(90),S(90)
IF ((A.LE.P(1)) .AND. (B.LE.T(1))) GOTO 13
IF ((A.GE.P(N)) .AND. (B.GE.T(N))) GOTO 14
IF ((A.LE.P(1)) .AND. (B.GE.T(M))) GOTO 15
IF ((A.GE.P(N)) .AND. (B.LE.T(N-M+1))) GOTO 16
IF (A.LE.P(1)) GOTO 19
IF (A.GE.P(N)) GOTO 23
MP = M+1
GOTO 17
23  I = (N-M+1)
I2= N
GOTO 22
19  I = 1
I2= N
22  DO 20 J=I,I2
20  IF (B.LE.T(J)) GOTO 21
21  J =J-1
DFUN2= S(J)+(B-T(J))/(T(J+1)-T(J))*(S(J+1)-S(J))
RETURN
13  DFUN2 = S(1)
RETURN
14  DFUN2= S(N)
RETURN
15  DFUN2=S(M)
RETURN
16  DFUN2=S(N-M+1)
RETURN
17  DO 3 I= MP,N,M
IF (A.LT.P(I)) GOTO 4
3  CONTINUE
4  IF (B.LT.T(I-M)) GOTO 9
IF (B.GT.T(I-1)) GOTO 11
GOTO 12
9   YT1= S(I-M)
YT2= S(I)
GOTO 18
11  YT1= S(I-1)
YT2= S(I+M-1)
GOTO 18
12  J1=I-M
J2=I-1
DO 5 J=J1,J2
IF (B.LT.T(J)) GOTO 6
5  CONTINUE

```

```

6      YT1= S(J-1) +(B-T(J-1))/(T(J)-T(J-1))*(S(J)-S(J-1))
I2=I+M-1
DO 7 J=I,I2
IF (B.LT.T(J)) GOTO 8
CONTINUE
7      YT2= S(J-1)+(B-T(J-1))/(T(J)-T(J-1))*(S(J)-S(J-1))
8      DFUN2= YT1+(A-P(I-1))/(P(I)-P(I-1))*(YT2-YT1)
18      RETURN
END
*****
*-----*
* SUBROUTINE FOR MATRIX INVERSION
*-----*
SUBROUTINE INVDET(C,N,DTNRM,DETM)
DOUBLE PRECISION C(11,11),J1(100),PD,DD,CC,S,DETM,DTNRM
PRINT*, '**C(1,2)',C(1,2)
PD=1.0D+00
DO 124 L=1,N
DD=0.0D+00
DO 123 K=1,N
123  DD=DD+C(L,K)*C(L,K)
DD=DSQRT(DD)
124  PD = PD*DD
DETM=1.0D+00
DO 125 L=1,N
125  J1(L+20)=L
DO 144 L=1,N
CC=0.0D+00
M=L
DO 135 K=L,N
135  CONTINUE
IF ((DABS(CC)-DABS(C(L,K))).GE.0.0D+00) GOTO 135
126  M=K
CC=C(L,K)
135  CONTINUE
127  IF(L.EQ.M) GOTO 138
128  K=J1(M+20)
J1(M+20)=J1(L+20)
J1(L+20)=K
DO 137 K=1,N
S=C(K,L)
C(K,L)=C(K,M)
137  C(K,M)=S
138  C(L,L)=1.0D+00
DETM=DETM*CC
DO 139 M=1,N
C(L,M)=C(L,M)/CC
139  CONTINUE
DO 142 M=1,N
IF (L.EQ.M) GOTO 142
129  CC=C(M,L)
IF (CC.EQ.0.0D+00) GOTO 142
130  C(M,L)=0.0D+00

```

```
141 DO 141 K=1,N
142 C(M,K)=C(M,K)-CC*C(L,K)
144 CONTINUE
144 CONTINUE
144 DO 143 L=1,N
144 IF (J1(L+20).EQ.L) GOTO 143
131 M=L
132 M=M+1
132 IF (J1(M+20).EQ.L) GOTO 133
136 IF (N.GT.M) GOTO 132
133 J1(M+20)=J1(L+20)
163 DO 163 K=1,N
163 CC=C(L,K)
163 C(L,K)=C(M,K)
163 C(M,K)=CC
163 J1(L+20)=L
143 CONTINUE
143 DETM=DABS(DETM)
143 DTNRM=DETM/PD
143 RETURN
143 END
*****
```

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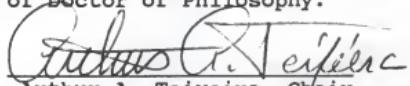
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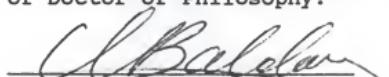
BIOGRAPHICAL SKETCH

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


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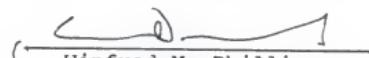
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